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Contents of Volume

Number 1

The electrochemistry of short-lived intermediate species 1
V A Benderskii, A G Krivenko

The parameters of the ^{13}C NMR spectra of substituted acetylenes: relation with electronic structure and reactivity 23
A G Proidakov, G A Kalabin, S F Vasilevskii

Periodicity of the change in properties in the series of *d*- and *f*-elements 39
G V Ionova

Specific features of the chemical structure of the oxo-complexes of d^0 and d^2 metals with monodentate and polydentate ligands 52
M A Porai-Koshits, V S Sergienko

The mechanism of the dehydration of alcohols and the hydration of alkenes in acid solution 63
M I Vinnik, P A Obraztsov

Polymeric composite materials reinforced with polyacrylonitrile fibres 78
S E Artemenko, L P Nikulina

β-Fluoro-substituted aminoacids 89
V P Kukhar', Yu L Yagupolskii, V A Soloshonok

Number 2

Laser-induced chemical deposition from the gas phase 103
V V Teslenko

Current state of the problem of aromaticity 116
M V Gorelik

Present ideas on the influence of the medium on acid–base equilibria. Hydrogen bonds in the gas phase and in solution 134
L M Epshtein, A V Iogansen

Enantioselective effects in coordination compounds 152
A A Kurganov, T M Ponomareva, V A Davankov

The photochemistry of azines 164
Ya N Malkin, V A Kuz'min

Recent trends in the theory of the deamination of aliphatic and alicyclic amines 179
A V Manuilov, V A Barkhash

Structural features and reactivity of tetrahalomethanes 193
B V Timokhin

Number 3

High speed autowave reaction regimes in low-temperature solid state chemistry 205
V V Barelko, I M Barkalov, V I Gol'danskii, A M Zanin, D P Kiryukhin

The structure and properties of complexes simulating molecular recognition 219
O A Raevskii

Reactions involving the heterolytic cleavage of carbon–element σ-bonds by Grignard reagents 234
Yu N Polivin, R A Karakhanov, V N Postnov

Reactions of phosphorus(III) chlorides with carbonyl compounds 251
M B Gazizov, R A Khairullin, V V Moskva

The azinyl–azinylidene tautomerism of azinylmethanes and general problems of the tautomerism of azines 268
V V Lapachev, O P Petrenko, V P Mamaev

Neutral acyclic analogues of crown-ethers and cryptands and their complex-forming properties 283
T E Kron, E N Tsvetkov

The use of microorganism cells immobilised in carrageenan for the synthesis of organic substances 299
T I Davidenko, G I Bondarenko

Number 4

Organic and molecular ferromagnetics: advances and problems 307
A L Buchachenko

The conformational analysis of organoelemental and organometallic molecules 320
T V Timofeeva, Yu T Struchkov

Carbon dioxide in coordination chemistry and catalysis 344
I S Kolomnikov, T V Lysyak

Control of the efficiency, selectivity, and capacity in single-column capillary gas chromatography 361
M Kh Lunskii

The synthesis and properties of thioaldehydes 378
V A Usov, L V Timokhina, M G Voronkov

Advances in the chemistry of sulphenic acid amides 396
I V Koval'

Number 5

New advances in the chemistry of thiirans 405
A V Fokin, M A Allakhverdiev, A F Kolomiets

The synthesis and properties of *N*-(2,3-epoxypropyl)carbazoles and the oligomers based on them 425
Kh M Akhmedov, Kh S Karimov, I M Shcherbakova, Yu N Porshnev, M I Cherkashin

The improvement of oxidation catalysts 440
L Ya Margolis, A A Firsova

Cement-containing catalysts 450
V I Yakerson, E Z Golosman

Progress in the synthesis of grafted materials using radiation graft polymerisation 469
L P Krul', A P Polikarpov

Inhibitors of the lipoxygenase conversion of polyenoic acids 482
D A Zabolotskii, G I Myagkova, R P Evstigneeva

Number 6

Selective replacement of hydrogen at a saturated carbon atom under the action of oxidising agents 501
L S Boguslavskaya, A V Kartashov, N N Chuvatkin

Reactions of pyridines, pyrimidines and 1,3,5-triazines with nucleophilic reagents 514
N V Alekseeva, L N Yakhontov

Generation and reactions of silylenes in the gas phase 531
E A Chernyshev, N G Komalenkova

Cyclic mono- and diphosphazenes 538
R I Tarasova, V V Moskva

Perfluorinated carbon-chain copolymers with functional groups and cation exchange membranes based on them: synthesis, structure and properties 560
Yu E Kirsh, S A Smirnov, Yu M Popkov, S F Timashev

αββ-Trifluorostyrene and polymers based on it 575
T S Nikitina

Number 7

Crystal chemistry at the present stage 591
P M Zorkii

X-Ray diffraction studies on electron density in organic crystals 592
P M Zorkii, A E Masunov

Low-temperature X-ray diffraction analysis: possibilities in the solution of chemical problems 607
M Yu Antipin

Characteristic features of the crystal chemistry of lanthanide molybdates and tungstates 627
V A Efremov

Structure of the uncharged, anionic, and cationic forms of aminoalkylcarboxylic and aminoalkylphosphonic complexones 643
L M Shkol'nikova, M A Porai-Koshits

Spiropyrans: structural features and photochemical properties 663
S M Aldoshin

The structure of novel conductive dithiolate complexes 686
V E Shklover, S S Nagapetyan, Yu T Struchkov

Number 8

Solubility of oxygen in electrolyte solutions 707
A Sh Groisman, N E Khomutov

Interaction of uranium oxides with dinitrogen tetroxide 728
L V Kobets, G N Klavsut'

Layered compounds of alkali metals in graphite in fine organic synthesis 738
V V Aksenov, V M Vlasov, G N Shnitko

Introduction of a carbon–carbon bond into electron-deficient aromatic compounds 750
G A Artamkina, S V Kovalenko, I P Beletskaya, O A Reutov

Thermal reactions of thiyl radicals 778
M G Voronkov, E N Deryagina

Polymer photostabilisers. Photophysical properties and stabilising efficiency 792
V G Plotnikov, A A Efimov

β-Aminophosphonates and β-aminophosphinates, synthesis, and properties 807
E S Gubnitskaya, L P Peresypkina, L I Samarai

Number 9

Progress in the chemistry of sulphilimines 819
I V Koval'

Sulphenamides and their derivatives 832
K A Petrov, G V Rudnev, V D Sorokin

Deoxygenation of coordinated and free sulphoxides 844
V Yu Kukushkin

Activation of the C–H bond by metal complexes 853
A E Shilov, G B Shul'pin

Polycondensation and polyaddition processes using silylated monomers 868
A L Rusanov

Aromatisation of low-molecular-weight paraffins on pentasil group zeolites 885
Kh M Minachev, A A Dergachev

α-Fluoroacrylates: synthesis, properties and use 906
L S Boguslavskaya, I Yu Panteleeva, T V Morozova, A V Kartashov, N N Chuvatkin

DMITRII YAKOVLEVICH TOPTYGIN (20th October 1931–20th May 1990) 918
P M Valetskii

Number 10

Chemistry of the atmosphere 919
Yu N Molin

Chemistry of the atmosphere and the climate 920
K Ya Kondrat'ev

The chemistry of OH and HO_2 radicals in the earth's atmosphere 928
Yu M Gershenzon, S G Zvenigorodskii, V B Rozenshtein

Expert evaluation of kinetic data for use in research on atmospheric modelling 945
J A Kerr

Problems of the distribution of the global aerosol 959
R Jaenicke

Catalytic methods for lowering the amount of nitrogen oxides in exhaust gases on combustion of fuel 973
Z R Ismagilov, M A Kerzhentsev, T L Susharina

Procedures for making gaseous industrial waste safe 989
Yu Sh Matros, A S Noskov

Number 11

Heterogeneous processes in the Earth's atmosphere and their ecological consequences 1007
Yu M Gershenzon, A P Purmal'

Mathematical modelling in problems of the chemistry of the atmosphere 1024
V V Penenko, G I Skubnevskaya

Emission of toxic metals into the atmosphere and their accumulation in the surface layer of the Earth 1037
S G Malakhov, E P Makhon'ko

Determination of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls and chlorine-containing pesticides in the environment 1051
A K Prokof'ev

Dioxins: analytical chemical aspects of the problem 1063
L A Fedorov, B F Myasoedov

Modelling of metal complexes by the method of molecular mechanics 1093
D V Pozigun, V E Kuz'min, G L Kamalov

The use of Langmuir – Blodgett films as recording layers in optical information carriers 1106
O V Chechel', E N Nikolaev

Number 12

Metal complex catalysis 1117
G V Lisichkin, A Ya Yuffa

Activation of C–C bonds in unsaturated hydrocarbons by metal complexes 1118
I S Akhrem, M E Vol'pin

Metal complex catalysis of oxidation reactions: principles and problems 1133
I I Moiseev, M N Vargaftik

Metal complexes of macrocycles in catalysis 1150
K B Yatsimirskii

Catalysis by metal complexes in organoaluminium synthesis 1157
U M Dzhemilev, O S Vostrikova, G A Tolstikov

Key steps in the cross-coupling of organometallic compounds with organic halides, catalysed by nickel and palladium compounds 1174
N A Bumagin, I P Beletskaya

Metal complex catalysis in the chemistry of solid organic raw material 1185
B N Kuznetsov

Metal-complex catalysis of the polymerisation of α-olefins 1193
B A Krentsel', L A Nekhaeva

Some of the most significant results in the field of catalysis by metal complexes (an expert assessment) 1208
G V Lisichkin, A Ya Yuffa

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The electrochemistry of short-lived intermediate species

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ABSTRACT. The results of the study of the electrode reactions of hydrogen atoms, simple organic radicals, and ions with anomalous valence by pulse radiolysis and laser photoelectron emission from the metal into the solution have been reviewed.

The bibliography contains 119 references.

Contents

I.	Introduction	1
II.	Generation of short-lived intermediate species	2
III.	Kinetics of the change in the current of electrode reactions	2
IV.	Polarograms of the species generated by a variable photoelectron emission current	5
V.	Time-resolved polarograms of intermediate species	6
VI.	Electrode reactions of hydrogen atoms	7
VII.	Intermediate species of the electrochemical carbon cycle	10
VIII.	Electrochemistry of alkyl and hydroxylalkyl radicals	13
IX.	The pK scale for weak CH-acids	15
X.	Intermediate species of the electrochemical nitrogen cycle	16
XI.	Reduction of ions with anomalous valence	19
XII.	Summary	20

I. Introduction

Most electrochemical processes are many-electron processes consisting of a sequence of one-electron stages in which intermediate species (IS) are formed and undergo further transformations. Since these species usually have a higher free energy than the reagents and products, their formation determines the energy barrier of the process as a whole, characterised by the magnitude of the overvoltage. Thus the electrochemistry of IS is a necessary part of modern electrochemistry, just as the study of the chemical transformations of IS forms part of chemical kinetics in general. Since IS take part in electrode reactions and are present in the adsorbed state on the electrode or diffuse to it from the layer of the solution next to the electrode, in the electrochemistry of short-lived IS, methods making it possible to determine the concentration or the current of the electrode reactions of the IS immediately after their generation are used. Extensive use is made of non-stationary electrochemical methods in which the IS are generated by an initial current pulse, and their subsequent transformations are recorded from the changes in the current and the electrode potential. These methods have been used to study a large number of reactions of free radicals and ions with anomalous valence (see in particular the published review[1]) with characteristic transformation times greater than $10^{-3}-10^{-4}$ s. The study of more rapid processes involving IS is restricted by the electrical double layer charging currents with change in potential. This restriction has stimulated the development of the methods of pulse electrochemical radiolysis (PECR) and laser photoelectron emission from the metal into the electrolyte solution (LPE), in which the IS are generated at a constant electrode potential. The present review examines the principles of these new methods and summarises the main results of their application. Particular attention is paid to the LPE method, since PECR data have already been reviewed.[2,3]

The sequence of processes taking place in a solution after pulse photoelectron emission from a metal has now been studied in sufficient detail.[4,5] The emitted electrons, which usually have energies in the range 0.5–2 eV, are thermalised and hydrated in aqueous solution, and the hydrated electrons (e^-_{aq}) are situated at a distance $l \simeq 3$ nm from the electrode surface. These electrons either diffuse to the electrode and are returned to the metal or are captured by an acceptor added to the solution, forming IS in a layer with approximately the same dimensions next to the electrode. As a result of these rapid processes, which with nanosecond duration bring about the photo-emission of laser pulses, a source of IS is formed close to the electrode; these IS diffuse to the electrode and take part in electrode reactions, accompanied by a change in the current or potential. The kinetics of this change are determined directly by the rate constants of the electrode reactions, so that it is possible to measure their absolute values up to 10^8 s^{-1}. The absence in the LPE method of the diffusion restrictions characteristic of electrochemical measurements is due to the small size of the IS source, noted above. Another characteristic of the method is that the rate constants are measured at a small degree of coverage, independent of potential, of the surface by the IS, the quantity of which is controlled by the intensity of the laser pulses and usually does not exceed 10^{11} cm^{-2}. Despite the small magnitude of the emitted charge, the pulse currents in LPE are fairly high ($\gtrsim 10^{-1}$ A cm^{-2}), so that the influence of contaminants is less significant than in ordinary electrochemical measurements at low overvoltages.

While the rates of the generation of the IS are similar in the LPE and PECR methods, the first of these has two important advantages: the absence of interfering reactions of primary radiolysis products (primarily hydrogen peroxide) and diffusion restrictions. In PECR, as a result of the uniform generation of IS in the bulk of the solution, their currents are restricted by diffusion and bulk recombination, so that it is possible to measure the rate constants only in a comparatively narrow range from 10^3 s^{-1} to 10^5 s^{-1}. In the LPE method, as shown below, it is possible to measure constants in the range 10^0-10^7 s^{-1}.

The idea of using pulse photo-emission measurements to study the fast electrode reactions of IS was put forward as early as 1971,[6,7] but it was only several years later[8,9] that apparatus was developed for quantitative measurements.

II. Generation of short-lived intermediate species

By using radiation-chemical data[10,11] to select an acceptor, it is possible to obtain most IS of many-electron electrode processes, so that the PECR and LPE methods are universal. Table 1 gives the rate constants k_a of the reactions yielding the IS whose electrochemistry has been studied by LPE. When it is difficult to select an acceptor of e^-_{aq} to obtain a required species, as for example in the case of hydroxyalkyl radicals, use is made of the reactions of OH radicals and H atoms previously generated in the solution by the reaction of e^-_{aq} with nitrous oxide and hydrogen ions respectively. The reactions listed in Table 1 have been studied by pulse radiolysis with identification of the IS from the absorption spectra. Most IS have also been identified from the EPR spectra of irradiated frozen solutions of the corresponding acceptors.

Table 1. Rate constants for the reactions of IS formation, studied by LPE methods.[10]

a) Reactions involving e^-_{aq} acceptors

IS	Acceptor	$10^{-9}\,k_a$, $mol^{-1}\,s^{-1}$	IS	Acceptor	$10^{-9}\,k_a$, $mol^{-1}\,s^{-1}$
H	H_3O^+	8	$CFCl_2$	$CFCl_3$	16
OH	N_2O	6	CF_3	CF_3Cl	7
CH_3	CH_3Cl	1.1	CCl_3	CCl_4	30
C_2H_5	C_2H_5Cl	0.8	C_2H_4Cl	$C_2H_4Cl_2$	9
n-C_3H_7	**n-C_3H_7Cl**	0.7	HCO	H_2CO_2	0.2
n-C_4H_9	**n-C_4H_9Cl**	0.4	$(CH_3)_2COH$	$(CH_3)_2CO$	6
C_6H_5	C_6H_5Br	4	CO_2^-	CO_2	8
CH_2Cl	CH_2Cl_2	6	NO_3^{2-}	NO_3^-	11
$CHFCl$	$CHFCl_2$	3	NO_2^{2-}	NO_2^-	4
CHF_2	CHF_2Cl	3	NO^-	NO	30
$CHCl_2$	$CHCl_3$	30	NH_2	NH_2OH	0.9
CF_2Cl	CF_2Cl_2	14	BrO_2	BrO_3^-	3

b) Reactions involving OH acceptors

IS	Acceptor	$10^{-9}\,k_a$, $mol^{-1}\,s^{-1}$	IS	Acceptor	$10^{-9}\,k_a$, $mol^{-1}\,s^{-1}$
CH_2OH	CH_3OH	0.6	$CH_2CH(OH)Cl$	C_2H_3Cl	7
CH_2CH_2OH	C_2H_4	3	CO_2^-	HCO_2^-	3
CH_3CHOH	C_2H_5OH	2	NH_2O	NH_2OH	9

III. Kinetics of the change in the current of electrode reactions

The changes with time in the current or emitted charge in LPE are calculated by solving the non-stationary equations for the diffusion of e^-_{aq} and the IS. A detailed analysis has been published.[5,12,13] The concentration of e^-_{aq} is given by the equation

$$\partial n/\partial t = D_e\partial^2 n/\partial x^2 - k_a N_a n + \frac{I_0}{l}\exp(-x/l)\,f(t), \qquad (1)$$

where D_e is the diffusion coefficient of e^-_{aq}; k_a the rate constant of the capture of e^-_{aq} by the acceptor added to the solution to give a concentration N_a; I_0 the photo-emission current generated by the laser pulse, whose form is described by the time function $f(t)$; and l the characteristic dimension of the source of e^-_{aq}. Because of the high rate of the electrode reaction of e^-_{aq}, the quantity $n(0, t) = 0$. For the concentration of IS stable† in solution $n_1(x, t)$, the following equation is applicable:

$$\partial n_1/\partial t = D\partial^2 n_1/\partial x^2 + k_a N_a n. \qquad (2)$$

As a result of their diffusion, a flux of IS into the adsorption plane $x = 0$, equal to $\kappa_a n_1(0, t)$, is created, where κ_a is the rate constant of the adsorption, with dimensions cm s^{-1}. The adsorbed species are desorbed with a rate constant W_d and take part in the electrode reactions with an overall rate constant $W = W_2 + W_3$ (W_2 and W_3 are the rate constants of the oxidation and reduction of the IS respectively). The surface concentration of IS (Γ) obeys the equation

$$d\Gamma/dt = \kappa_a n_1(0, t) - (W_d + W)\Gamma. \qquad (3)$$

As a consequence of the continuity of the flux at $x = 0$ there arises the boundary condition

$$D(\partial n_1/\partial x)_{x=0} = \kappa_a n_1(0, t) - W_d\Gamma. \qquad (4)$$

This adsorption–desorption scheme for the electrochemically active IS is applicable if the degree of coverage is small, that is κ_a and W_d are independent of Γ. If the rate constant W is smaller than the rate of the processes involving e^-_{aq} and the reciprocal of the laser pulse duration t_0^{-1}, that is

$$W < D_e/l^2,\ k_a N_a,\ t_0^{-1}, \qquad (5)$$

the equation for the change in the current with time is independent of the duration of the laser pulse, the characteristic length of the source l, and the rate of capture of e^-_{aq}. From the solution of Eqns. (1) and (2) it follows[13] that the form of the kinetic curves of the charge emitted into the solution $Q(t)$ is determined by the parameter

$$\xi = 4\kappa_a W/W_d^2 D \qquad (6)$$

and, depending on its value, is described by one of the following relationships ($t > t_0$):

$$Q/Q_m = \begin{cases} 1 + \dfrac{W_3 - W_2}{W_3 + W_2}(1 - \exp(-Wt)), & \xi \gg 1; \\ 1 + \dfrac{W_3 - W_2}{W_3 + W_2}\left(1 - \dfrac{1}{\varkappa}\sqrt{\dfrac{D}{\pi t}}\right), & \xi \ll 1,\ \varkappa\sqrt{t/D} > 1, \end{cases} \qquad (7)$$

where Q_m is the number of e^-_{aq} captured by the acceptor, and κ the effective rate constant of the electrode reaction, determined by the quasi-stationary current

$$\varkappa = \kappa_a \frac{W}{W + W_d}. \qquad (8)$$

The rate constants for the adsorption and desorption are related by the detailed equilibrium condition

$$\frac{\kappa_a}{W_d} = \frac{\Gamma_0}{N_0}\exp\left(-\frac{\Delta G_a^0}{RT}\right), \qquad (9)$$

where ΔG_a^0 is the free energy of adsorption, corresponding to the selected standard bulk (N_0) and surface (Γ_0) concentrations. With allowance for Eqn. (9), the condition $\xi \gg 1$ means that the kinetic

† The case in which the IS is transformed in the bulk has been examined.[7] The stability of the IS means that the time of their homogeneous transformation is greater than the time of their movement to the electrode.

curves $Q(t)$ have an exponential form in the following range of values of W:

$$\frac{\varkappa_a^2}{D} > W > \frac{D}{4}\left(\frac{N_0}{\Gamma_0}\right)^2 \exp\left(\frac{2\Delta G_a^0}{RT}\right) = W_{\min}. \quad (10)$$

The upper boundary of the range is determined by the condition that W be small compared with the rate of adsorption. The opposite inequality corresponds to diffusion-controlled reactions, whose rate is limited by the transport of the reagent to the surface. The values of W in this case are greater than 10^8 s^{-1}, and cannot be measured by the LPE method, since the conditions (5) do not apply. The lower boundary depends on ΔG_a^0, and for $\Delta G_a^0 < -25$ kJ mol^{-1} does not exceed 1 s^{-1} for the following typical values of the other parameters: $N_0 = 64 \times 10^{20}$ cm^{-3} (standard 1 M solution), $\Gamma_0 = 10^{14}$ cm^{-2}, $D = 10^{-5}$ cm^2 s^{-1}, $T = 300$ K. Estimation of $W_{\min}$ shows that even for comparatively weakly adsorbed IS, the range of values of W satisfying relationship (10) is greater than $10^7 - 10^8$. When condition (10) is satisfied, there is no adsorption equilibrium, and the IS are not desorbed and take part in electrode reactions. Otherwise, when $\xi \ll 1$, adsorption equilibrium is established, the form of the kinetic curves changes, and $Q(t)$ is characterised by the effective rate constant κ, as in ordinary electrochemical measurements, under the conditions of a quasi-stationary current: $j_c = \kappa n_1(0)$. The range of values of κ that can be measured is restricted by the condition

$$\varkappa < \sqrt{W_{\min} D},\ \sqrt{k_a N_a D},\ \sqrt{D/t_0},\ D/l \quad (11)$$

from which it follows that the LPE method can be used to measure the rate constants of the electrode reactions of non-adsorbed IS ($\Delta G_a^0 \geqslant 0$) up to 30–50 cm s^{-1}.

It follows from conditions (7) that the kinetic curves $Q(t)$ are determined by the existence of two signals: the initial rapid signal corresponding to the photo-emission and return to the electrode of the e_{aq}^- not captured by the acceptor, and the subsequent slower signal due to the electrode reactions of the IS. The ratio of the amplitudes of these signals equal to $Q(t)/Q_m - 1$ as $t \to \infty$ corresponds to the number of electrons transferred from the metal to the solution, calculated for one electron captured by the acceptor, that is for one IS, so that $Q(\infty)/Q_m - 1$ is the order (n) of the electrode reaction

$$X + n e^- \rightarrow X^{n-} \quad (12)$$

with respect to electrons. The values of n, unlike W, can also be determined by measuring the relative values of the photo-current for stationary photo-emission into the solution being studied and into a solution for which n is known.[4,5] The latter are usually N_2O solutions, in which the capture of e_{aq}^- gives OH radicals, produced throughout the working range of the mercury electrode, so that $n = 1$.

$Q(t)$ is measured using the laser electrochemical relaxometer[5,9,14,15] (Fig. 1). The nitrogen laser with a wavelength of 337 nm, the fourth harmonic of the neodymium laser (265 nm), and excimer lasers (220 nm and 248 nm) [15] are used as light sources. To avoid the superposition of effects due to pulse heating to the electrode, the production of capillary waves (in the case of liquid metal electrodes), and decrease in the concentration of the acceptor in the layer next to the electrode, the light intensity is restricted to 700 kW cm^{-2} for a pulse duration of $\sim 10^{-8}$ s. The range 20–200 kW cm^{-2} is most convenient for the measurements. The restriction of the light intensity and the low quantum yield of the photo-emission ($\sim 10^{-4}$ A W^{-1}) make it necessary to record the weak signals in a broad frequency band. It is most convenient to use a stroboscopic recording scheme, employing laser pulses with a repetition frequency of 6–25 Hz and a signal measured at a given moment of time (relative to the laser pulse) and a given electrode potential. The signal recording time is 30–40 s, so that it is possible to average over a large number ($\sim 10^3$) of pulses. With time scanning, the relaxometer can be used to obtain the kinetic curves $Q(t)$, and when the potential E is scanned, it gives the $Q(E)$ relationship at the selected moment of time. A design feature of the cell with the mercury electrode, ensuring suppression of capillary waves, is the use of a photocathode with a flat mercury surface which is kept in an amalgamated platinum capillary and is replaced after each scanning cycle.

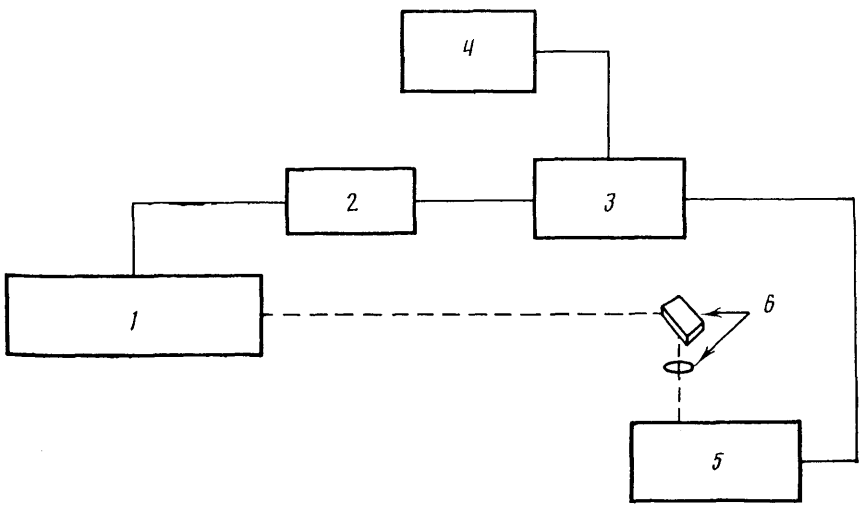


Figure 1. Block diagram of the laser electrochemical relaxometer: *1*, photon generator; *2*, synchronisation system; *3*, stroboscopic oscillograph; *4*, recorder; *5*, measuring cell with amplifier and polarisation scheme; *6*, laser beam focussing system.

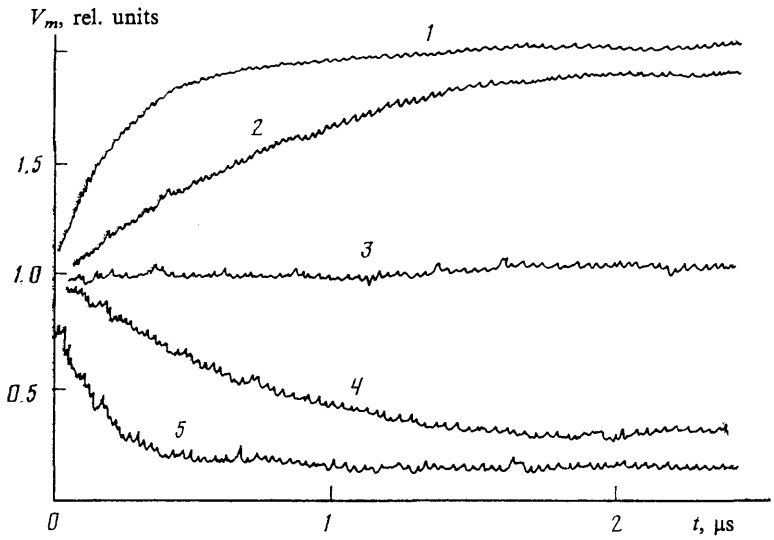


Figure 2. Kinetic curves for the electrochemical reduction and oxidation of H atoms in 1 M aqueous KCl solution with the addition of 0.1 M HCl at different values of the potential of the mercury electrode, V: *1*, −0.9; *2*, −0.7; *3*, −0.55; *4*, −0.5; *5*, −0.4.

The recorded signal $V(t)$ is equal to the variation in the electrode potential brought about by the change in its charge, and is given by the relationship[5]

$$V(t) = \frac{1}{C}\int_0^t \frac{dQ(t')}{dt'} \exp\left(-\frac{t-t'}{\tau_0}\right) dt', \qquad (13)$$

where C is the capacity of the electrical double layer; $\tau_0 = RC$ the time constant of the electrochemical cell and the input circuit; and R their total ohmic resistance. From Eqns. (7) (for $\xi \gg 1$) and (13) it follows that

$$\frac{V}{V_m} = \frac{2W_3\tau_0 - 1}{W\tau_0 - 1} \exp(-t/\tau_0) - \frac{(W_3 - W_2)\tau_0}{W\tau_0 - 1} \exp(-Wt), \; t \gg t_0, \qquad (14)$$

where $V_m = Q_m/C$. For $W\tau_0 \gg 1$, $V(t) = Q(t)/C$. These charge measurement conditions are used for values of W from 10^7 s^{-1} to 10^4 s^{-1}, since τ_0 is usually equal to $10^{-3}-10^{-4}$ s. The rate constants of slower reactions are measured using current conditions in which $W\tau_0 \ll 1$ and

$$V/V_m = \exp(t/\tau_0) + (W_3 - W_2)\tau_0 \exp(-Wt). \qquad (15)$$

To extend the range of measurement of the constants under current conditions, τ_0 is decreased, and t_0 is increased. The use of current–voltage transformers with an input resistance close to zero decreases to τ_0 to 3–5 μs, so that the highest values of W that can be measured under current conditions are 10^5 s^{-1}.[16] $W \leqslant 10^3$ s^{-1} are measured using the pulses of a continuous helium–cadmium laser (λ = 325 nm) produced by a mechanical modulator; periodic illumination methods are also used.[17] The combination of the two measurement conditions (charge and current) makes it possible to cover the range of values of W from 1 s^{-1} to 10^7 s^{-1}, satisfying the inequalities (10).

The kinetic curves are treated using relationships (14) and (15). The accuracy of the determination of W is restricted by the scatter in the amplitude of the laser pulses, and is generally 10–15%. Eqns. (7) show that the form of the kinetic curves deviates from the exponential for $\xi \simeq 1$. For electrode reactions whose characteristic time is less than 10^{-4} s, $\xi \leqslant 1$ at rates of desorption greater than 10^5 s^{-1}, that is in the case where there is practically no adsorption of the species ($\Delta G_a^0 > -10$ kJ mol^{-1}). Analysis of the $V(t)$ curves makes it possible not only to determine the absolute values of W or κ but also to establish the state (adsorbed or not) in which electron transfer takes place.

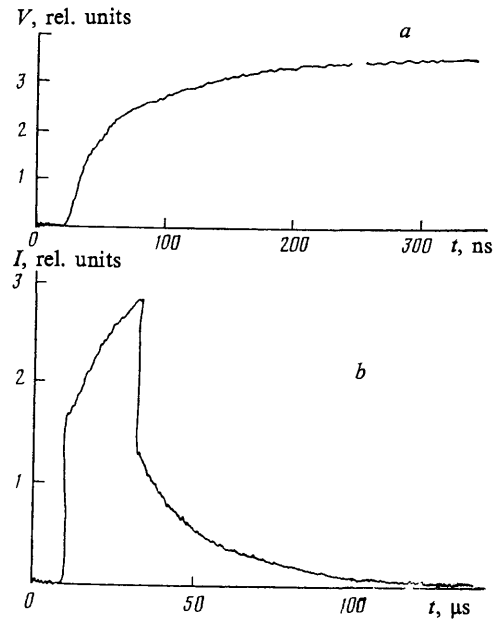


Figure 3. Form of the kinetic curves for the reduction of the Ch_2Cl radical adsorbed on a mercury electrode: *a*, under charge measurement conditions (E = −1.67 V, $W_3 = 1.4 \times 10^7$ s^{-1}), *b*, under current measurement conditions (E = −0.89 V, W_3 = 30 s^{-1}, laser pulse duration 20 ms).[16]

Typical $V(t)$ curves are given in Figs. 2 and 3. The changes in the form and characteristic times of these curves are due to the

changes in W_2 and W_3 with change in the electrode potential.‡ The rate of the rapid reactions of adsorbed hydrogen atoms are measured under charge conditions. In the cathodic potential range, in which the reduction of H atoms predominates, the $V(t)$ curves consist of a short initial section and a section corresponding to the slower doubling of the emitted (captured by the acceptor) charge ($W_3 \gg W_2$, $n = 1$). The characteristic rise time, that is W_3^{-1}, decreases with increase in $-E$. For anodic displacement of E, the rise time increases, and the amplitude in the "slow" section decreases. At the characteristic potential E^*, when the rate constants of the reduction and oxidation become equal:

$$W_2(E^*) = W_3(E^*) = W^*, \tag{16}$$

the "slow" section disappears, since when oxidation and reduction are equally probable (and when the values of n are identical), the transformations of the IS do not change the charge of the electrode. For $E > E^*$, the magnitude of $V(t)$ decreases from the initial value V_m to $V_m W_3/(W_2 + W_3)$, since the main channel for the transformation becomes the ionisation of H atoms, leading to the return to the electrode of the emitted electrons and the electrons captured by the acceptor ($n = -1$). The decay time of $V(t)$ decreases with increase in E as a result of the increase in W_2. Fig. 3 gives the $V(t)$ curves corresponding to the reduction of the CH_2Cl radical, for which the $W_3(E)$ relationship can be measured over a range of change in $W_3(E)$ of almost 10^7.

IV. Polarograms of the species generated by a variable photoelectron emission current

Varying illumination with a frequency of Ω creates an IS flux in phase with it, with a characteristic source length $l_1 \simeq \sqrt{D/k_a N_a} \simeq 10^{-5}-10^{-6}$ cm, so that at the low frequencies usually employed $l_1 \ll \sqrt{D/\Omega}$ and the resulting photo-emission current, as in the case where the inequalities (5) are satisfied, is independent of the conditions under which the IS are formed. Without forgetting that photoemission gives IS and not stable reagents, the obvious similarity in the methods used to observe the polarograms and the photocurrent should be emphasised. In polarography, a stationary flux of the reagent to the electrode is maintained by its constant concentration at the outer boundary of the Nernst layer (see for example the works by Bond[1] and Damaskin and Petrii[18]), and in the version of the LPE method being considered it is maintained by the constant amplitude of the current of the emitted electrons, which, like the diffusion polarographic current, determines the height of the polarographic wave. Although the reasons for the production of the limiting current are different in the two cases being considered, the polarisation dependence of the photocurrent coincides with the polarographic wave. The range of Ω suitable for observing the polarograms of IS is restricted by the conditions of small interfering charging currents and convective mixing of the layer with a thickness $\sqrt{D/\Omega}$:

$$\tau_0^{-1} > \Omega > D/\delta^2, \tag{17}$$

where $\delta \simeq 10^{-2}$ cm is the thickness of the Nernst layer in the absence of forced mixing. The range of electrode reaction rate constants ($\kappa \simeq \sqrt{D\Omega}$) that can be measured in this range of Ω ($0.1-3 \times 10^3$ Hz) is $10^{-3}-1$ cm s^{-1}.

The form of the polarographic waves for a periodic photoemission current has been analysed.[17,19-22] The solution of Eqns. (1) and (2) under the conditions in which a periodic source is used shows that the amplitude and phase of the first harmonic of the photocurrent in the irreversible n-electron reduction of a non-adsorbed product of the capture of e_{aq}^- are given by the relationship

$$j = \frac{I}{I_0} = \left| 1 + n\frac{v_1}{v_1 + \sqrt{2i}} \right|, \quad \operatorname{tg}\Phi = -\frac{nv_1}{((1+n)v_1 + 1)(v_1+1)+1}, \tag{18}$$

where I is the measured photocurrent, I_0 the current for the formation of the IS, equal to the difference between the currents of the photoemission and the return to the electrode of the e_{aq}^- not captured by the acceptor, and $v_1 = \kappa_1\sqrt{2/D\Omega}$. When the rate constant of the reduction κ_1 obeys the equation of retarded discharge

$$\kappa_1 = \kappa_{10}\exp(\alpha\eta), \quad \eta = \frac{e}{kT}(E^0 - E), \tag{19}$$

(E^0 is the standard potential, and α the transfer coefficient), the $j(E)$ relationship has the form of a polarographic wave in which j increases from 1 to $1 + n$. The half-wave potential of the one-electron reduction, for which $j = 3/2$, is

$$E_{1/2} = E^0 - \frac{1}{2\alpha}\ln\left(0.91\frac{D\Omega}{\kappa_{10}^2}\right). \tag{20}$$

With increase in Ω, the potential $E_{1/2}$ increases in logarithmic proportion while the form of the wave is preserved. The slope of the wave in the region of $E_{1/2}$, equal to $(dj/dE)_{E=E_{1/2}}$, is independent of Ω and equal to $0.29\alpha kT/e$. The wave for the irreversible reduction of adsorbed IS is described by the relationships

$$j = \left| 1 + n\frac{W_3}{W_3 + i\Omega} \right|, \quad \operatorname{tg}\Phi = -\frac{n\Omega W_3}{(1+n)W_3^2 + \Omega^2} \tag{21}$$

and its slope in this case is approximately twice that for non-adsorbed species. The phase shift is greatest close to $E_{1/2}$, and is several times greater for adsorbed species than for non-adsorbed species. The wave for the reversible reduction of non-adsorbed IS ($X + ne^- \leftrightharpoons X^{n-}$) is described by the equation

$$j = \left| 1 + n\frac{v_1}{v_1 + v_2 + \sqrt{2i}} \right|. \tag{22}$$

Here, $v_2 = k_2\sqrt{2/D\Omega}$, where κ_2 is the rate constant of the back reaction of X^{n-} oxidation. The potential of the reversible half-wave is equal to the standard redox potential X^{n-}/X, and its slope is $nkT/4e$, like the slope of the usual reversible polarographic wave under stationary diffusion conditions.[18] The wave remains reversible, and $E_{1/2} = E^0$, when $\Omega \ll 2\kappa_{10}^2/D$. At higher values of Ω, the wave becomes irreversible, it is displaced along the E axis, its slope decreases, and a phase shift is produced. The characteristics of the E-waves for the one-electron reduction and oxidation of IS are summarised in Table 2.

The wave for the n-electron irreversible reduction with previous irreversible transformation of the primary IS ($X \rightarrow Y \rightarrow Y^{n-}$) is described by the relationship

$$j = \left| 1 + n\frac{v_1}{v_1 + \sqrt{2i}}\frac{\sqrt{\beta_1 + 2i} - \sqrt{2i}}{\sqrt{\beta_1 + 2i}} \right|. \tag{23}$$

Here, $\beta_1 = 2k_1/\Omega$, where k_1 is the rate constant of the homogeneous

‡ All the values of E except the standard values are given relative to the saturated calomel electrode.

reaction X → Y. As in the case of ordinary polarographic *CE*-waves, a limiting current determined by the rate of the chemical stage is produced. With increase in Ω, the height of the wave (the amplitude of the limiting current) decreases, and the wave is displaced to more negative potentials. When the chemical stage is reversible and the rate constant of the back reaction k_2 is appreciably greater than the rate constant of the homogeneous reaction k_1, the limiting current j_∞ is determined by the equilibrium constant of this stage:

$$j_\infty = \left| 1 + n \frac{p}{p + \sqrt{2i}} \right|, \text{ where } p = \frac{k_1}{k_2} \sqrt{\frac{k_1 + k_2}{\Omega}}. \quad (24)$$

As an example of a *CE*-wave, Fig. 4 gives the $j(E)$ relationships for the three-electron reduction of NO to NH_2OH. The reversible chemical stage preceding the electrode reaction is the protonation of NO in the presence ot NH_4^+ ions.[23]

Table 2. Characteristics of the *E*-waves of the one-electron reduction (oxidation) of the intermediate species generated by a periodic photoelectron emission current.[22]

Mechanism of reduction (oxidation)	Relationships		
	$\eta_{1/2}$ (Ω)	$(dj/d\eta)_{\eta=\eta'_{1/2}}$	$\operatorname{tg} \varphi_m^*$
$A \underset{(\varkappa_2)}{\overset{\varkappa_1}{\rightarrow}} B$	$a \ln\left(bD\Omega/\varkappa_0^2\right)$, where $a = \frac{1}{2}\alpha(\frac{1}{2}\beta)$, $b = 0.91$ (1.35)	0.294 α (0.282 β)	−0.143 (0.451)
$A_{ads} \underset{(W_3)}{\overset{W_3}{\rightarrow}} B$	$a \ln\left(b\Omega/W_0\right)$, where $a = 1/\alpha$ (1/β), $b = 0.84$ (1.73)	0.486 α (0.375 β)	−0.354 (1.73)
$A \underset{\varkappa_2(\varkappa_1)}{\overset{\varkappa_1(\varkappa_2)}{\rightleftarrows}} B$	0 (0)	0.25 (0.25)	$-0.17\sqrt{D\Omega/\varkappa_0^2}$ $\left(0.35\sqrt{D\Omega/\varkappa_0^2}\right)$
$A_{ads} \underset{W_3(W_3)}{\overset{W_3(W_3)}{\rightleftarrows}} B_{ads}$	0 (0)	0.25 (0.25)	$-0.17\,\Omega/W_0$ $(0.5\,\Omega/W_0)$
$A_{ads} \underset{\varkappa_2(\varkappa_1)}{\overset{W_3(W_3)}{\rightleftarrows}} B$	$a \ln\left(b\varkappa_0^2\Omega/W_0^2D\right)$, where $a = \frac{1}{2}(-\frac{1}{2})$, $b = 0.91$ (1.35)	0.291 (0.272)	−0.143 (0.451)
$A \underset{W_3(W_3)}{\overset{\varkappa_1(\varkappa_2)}{\rightleftarrows}} B_{ads}$	$a \ln\left(b\varkappa_0^2\Omega/W_0^2D\right)$, where $a = -\frac{1}{2}(\frac{1}{2})$, $b = 1.10$ (0.91)	0.291 (0.272)	0.143 (0.451)

* In oxidation reactions the phase shift reaches π/2. Here the values of tan ϕ for $E = E_{1/2}$ are given.

Since most IS are capable of undergoing both reduction and oxidation, the $j(E)$ relationships usually have the form of cathodic–anodic waves. For one-electron irreversible processes ($n = \pm 1$) involving non-adsorbed and adsorbed IS, their form is determined by the relationships:

$$j = \left| 1 + \frac{v_1 - v_2}{v_1 + v_2 + \sqrt{2i}} \right|, \quad \operatorname{tg} \Phi = -\frac{v_1 - v_2}{(2v_1 + 1)(v_1 + v_2 + 1) + 1}$$

or

$$j = \left| 1 + \frac{W_3 - W_2}{W_2 + W_3 + i\Omega} \right|, \quad \operatorname{tg} \Phi = -\frac{(W_3 - W_2)\,\Omega}{2W_3(W_2 + W_3) + \Omega^2} \quad (25)$$

The potential at which $j = 1$ is equal to E^*. The slope of the cathodic–anodic wave at $E = E^*$ is determined by the sum of the transfer coefficients

$$\left(\frac{dj}{dE}\right)_{E=E^*} = \frac{v^*(1 + 2v^*)}{(1 + 2v^*)^2 + 1}(\alpha + \beta)\frac{kT}{e} \text{ or}$$
$$\left(\frac{dj}{dE}\right)_{E=E^*} = \frac{2W^{*2}}{\Omega^2 + 4W^{*2}}(\alpha + \beta)\frac{kT}{e}. \quad (26)$$

Here, $v^* = \kappa^*\sqrt{2/D\Omega}$, where κ^* is the value of the constants for $E = E^*$, when the rates of oxidation and reduction are equal. According to Eqns. (26), as $\Omega \to 0$ the slope of the cathodic–anodic wave is equal to $(\alpha + \beta)kT/2e$ and decreases with increase in Ω. The wave is then split into separate cathodic and anodic components, and the difference in the half-wave potentials increases logarithmically. Splitting of the cathodic–anodic wave with increase in Ω has been observed for alkyl and hydroxyalkyl radicals.[24] The determination of the rate constants and transfer coefficients becomes possible in the split wave.

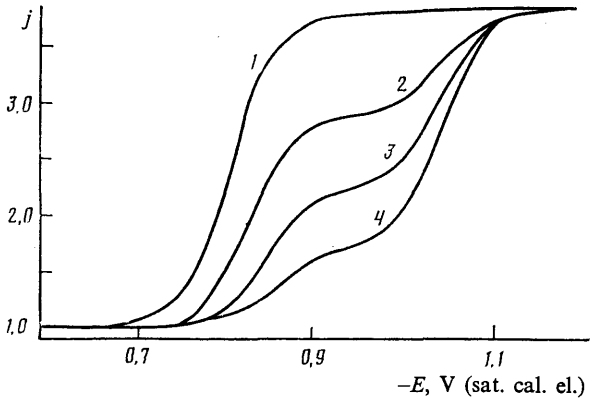


Figure 4. Polarograms for the three-electron reduction of NO, generated by a photoelectron emission current with a frequency of 1, 6.4, 29, and 87 Hz (curves *1*–*4* respectively) in aqueous 0.5 M Na_2SO_4 + 0.5 M $(NH_4)_2SO_4$ + 10^{-3} M $NaNO_2$.[23]

The analysis of the form and phase of the polarograms over a wide frequency range makes it possible to study fairly complex IS transformations.[22]

V- Time-resolved polarograms of intermediate species

The $Q(E)$ relationship at a fixed moment of time *t* for the one-electron reduction and oxidation of adsorbed IS has the form:[25]

$$q(\varphi, \tau) = \frac{Q(\varphi, \tau)}{Q_m} = 1 + (1 - \exp(-\tau(e^{\alpha\varphi} + e^{-\beta\varphi})))\operatorname{th}\frac{\alpha + \beta}{2}\varphi, \quad (27)$$

where

$$\varphi = \frac{e}{kT}(E^* - E), \quad \tau = W^*t,$$

and the rate constants of the oxidation and reduction are described by the equations for retarded discharge

$$W_2 = W^* \exp(-\beta\varphi), \quad W_3 = W^* \exp(\alpha\varphi). \tag{28}$$

Eqn. (27) describes a time-resolved cathodic–anodic wave. The quantity $q(\tau)$ is the number of electrons transferred to the solution, calculated for one IS at the moment of time t after its formation. If the species is not adsorbed, the $q(\varphi, \tau)$ relationship is described by the expression

$$q(\varphi, \tau) = 1 + (1 - w(a_1 (e^{\alpha\varphi} + e^{-\beta\varphi}))) \operatorname{th} \frac{\alpha+\beta}{2}\varphi, \tag{29}$$

where

$$w(z) = e^{z^2} \operatorname{erfc} z, \quad a_1 = \varkappa_a \frac{W^*}{W^* + W_d} \sqrt{\frac{t}{D}}. \tag{30}$$

It follows from Eqns. (27) and (29) that the splitting of the cathodic–anodic wave takes place in a narrow range $t^{-1} \sim W^*$. For $W^*t < 1$, two waves are observed with a section $q = 1$ close to E^*, which becomes narrower with increase in t. When $W^*t > 1$, one wave is produced

$$q_{in}(\varphi) = 1 + \operatorname{tn}\left(\frac{\alpha+\beta}{2}\varphi\right).$$

Fig. 5 gives the time-resolved polarograms for the CH_2OH radical. The asymmetry of the cathodic and anodic waves is due to the difference in the transfer coefficients for W_2 and W_3. If the electrode reactions are accompanied by the destruction of IS not associated with electron transfer, then the section $q = 1$ does not disappear even when $W^*t > 1$. This has been observed for CH_3 radicals,[24] whose recombination is more rapid than the electrode reactions in the region of E^*. As an example of the time-allowed polarogram of a many-electron reduction, Fig. 6 gives the $q(\varphi, \tau)$ relationships for the BrO_2 radical.[25] For $t = 0.25$ μs and 0.5 μs and $E \geqslant -0.9$ V, the radical is unable to undergo complete reduction to BrO_2^-, which is formed quantitatively at $E < -0.9$ V ($n = 1$). The bromite ion is reduced at $E < -1.15$ V. The extent of the reduction increases with increase in t and $-E$. At $t > 50$ μs, the waves for the reduction of BrO_2 and BrO_2^- are not resolved, and the overall five-electron wave for the formation of Br^- is observed.

The time-resolved polarograms obtained under charge measurement conditions can be used to study more rapid processes than when a periodic photoemission current is used.

Examples of polarograms obtained by the PECR method have been published.[2,3,26] Unlike the polarograms obtained by the LPE method, they show a broad range of E values in which $j = 0$, due to the more rapid recombination of the IS, compared with the electrode reactions.

VI. Electrode reactions of hydrogen atoms

The adsorbed hydrogen atom is an IS in the electrochemical liberation of hydrogen (ELH), which in the case of metals with a high overvoltage includes a stage involving the discharge of hydrogen ions

$$H^+(aq) + e^- \xrightarrow{\varkappa_1} H_{ads}, \tag{31}$$

the reverse ionisation stage

$$H_{ads} \xrightarrow{W_2} H^+(aq) + e^- \tag{32}$$

and electrochemical desorption, in which the proton donors (PD) are water molecules and hydrogen ions[18,27–29]

$$H_{ads} + H_2O + e^- \xrightarrow{W_{30}} H_2 + OH^- \tag{33}$$

$$H_{ads} + H^+(aq) + e^- \xrightarrow{W_{31}} H_2. \tag{34}$$

The detailed study of the polarisation relationships observed when low-frequency photocurrents ($W \gg \Omega$) are used in solutions of acids[4,5,30–33] has established that the value of E^* depends on the pH of the solution, since a linear relationship exists between the overall rate constant of the electrochemical desorption and the concentration of hydrogen ions (N_{H^+}):

$$W_3 = W_{30} + W_{31} N_{H^+}. \tag{35}$$

The sum of the transfer coefficients of reactions (32) and (34) at a mercury electrode was found to be close to 0.5. Since the transfer coefficient for the discharge of hydrogen ions (α_1) at high overvoltages is equal to 0.5 and is related to β by the detailed balance condition ($\alpha_1 + \beta = 1$), it follows from the photo-emission data that the value of α in electrochemical desorption reactions is small, that is these exothermic reactions are almost activationless.

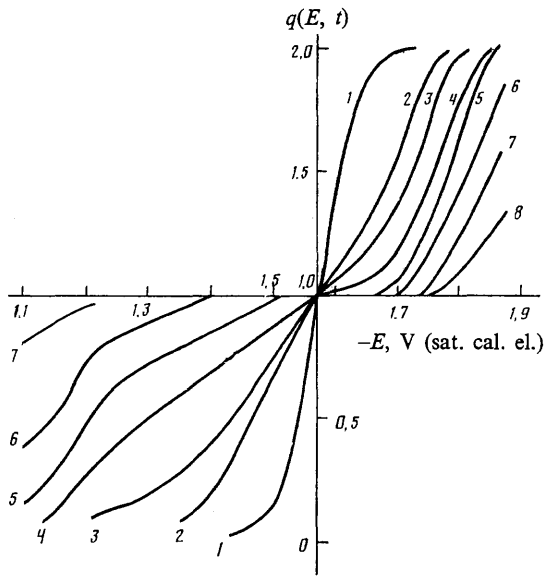


Figure 5. Time-resolved polarograms of the hydroxymethylradical adsorbed on a mercury electrode; photo-emission in 0.5 M KCl + 0.2 M CH_3OH + 2×10^{-2} M N_2O;[25] the curves correspond to the following instants of time, s: *1*, stationary; *2*, 10^{-4}; *3*, 5×10^{-5}; *4*, 2×10^{-5}; *5*, 10^{-5}; *6*, 5×10^{-6}; *7*, 2×10^{-6}; *8*, 10^{-6}.

The first measurements of the absolute values of the rate constants of electrochemical desorption[8] showed that W_3 is about 10^6 s^{-1}. Quantitative measurements have been carried out.[31,34–36] The kinetic curves $Q(t)$ are exponential, that is the hydrogen atoms take part in the electrode reactions after adsorption. The overall rate constant is described by Eqn. (35). The values of W_{30} and W_{31} are given in Table 3. It has been found[33,34] that the rate constant of reaction (34) on mercury and bismuth shows an exponential

dependence on the electrode potential, but is independent of temperature (Fig. 7). This relationship, which differs from that expected from the theory of retarded discharge, has been attributed[29,34,35] to the tunnel transfer of an electron from the metal to the reaction complex $H_{ads}-H_3O^+$. Since the change in the height of the barrier for electron tunnelling is equal to the change in the electrode potential, the rate constant of the tunnel electrode reaction shows an exponential dependence on E, but is independent of T. The electron transfer is accompanied by a simultaneous quantum displacement of the proton along the reaction coordinate, and this is the reason for the observed isotopic H/D effect. The model[34,35] predicts a decrease in W_{31} and an increase in the isotope effect with increase in both the energy of the M–H bond and the energy of reorganisation along the coordinate of the proton. The increase in the isotope effect on going from Hg to Bi and Ga (Table 3), when the energy of the bond between the H atom and the metal surface increases by 30–34 kJ mol,[37] is apparently due to the first of these factors, and the fact that the isotope effect is greater for Ga than for Bi indicates that reaction (34) involves a greater quantum displacement of the proton on the gallium electrode. This suggestion agrees with the high values of the isotope separation factors for hydrogen and tritium, characteristic of ELH reactions on Ga.[28] The measured values of W_{31} correspond to an electron tunnelling length of 4–5 Å for a height of the parabolic barrier of about 1.5 eV. The $W_{31}(E)$ relationship is described by the expression

$$W_{31}(E) = W_{31}(E^0)\exp\left(\frac{e(E^0-E)}{\gamma}\right), \qquad (36)$$

in which the value of γ is related to the tunnelling parameters of the electron and the proton. The values of γ for Hg, Bi, and Ga are 0.12, 0.18, and 0.17 eV respectively.

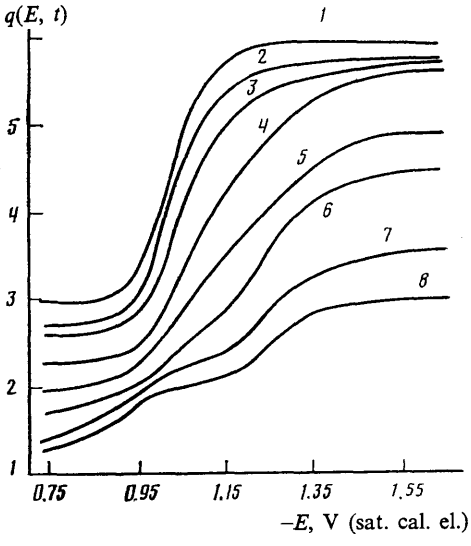


Figure 6. Time-resolved polarograms of the five-electron reduction of the BrO_2 radical in 0.5 M KCl + 10^{-2} M $KBrO_3$ solution;[25] the curves correspond to the following instants of time, s: *1*, stationary; *2*, 10^{-4}; *3*, 5×10^{-5}; *4*, 10^{-5}; *5*, 3×10^{6}; *6*, 10^{-6}; *7*, 0.25×10^{-6}.

The rate constant of reaction (33) depends little on E (Table 3), and its temperature dependence is characterised by an activation energy of ~15 kJ mol^{-1}, which remains unchanged in the electrode potential. The mechanism of this reaction has not been satisfactorily explained. From the value given for the activation energy, typical of dipole relaxation in water, and the times of this relaxation in the double layer ($10^{-8}-10^{-7}$ s),[38] it has been suggested[36] that the rate of reaction (33) is limited by the rate of the orientational rearrangement of the water molecules in the reaction complex. The values of W_{30} correspond to the bimolecular rate constants of reaction (33), which are ~10^{-3} times smaller than those for reaction (34).

Table 3. Rate constants of the electrochemical desorption of hydrogen and deuterium.[35,36]

Constant	Electrode	Value* of the constant at −E, V					
		0.9	1.0	1.1	1.2	1.3	1.4
$10^{-6}W_{30}$, s^{-1}	Ga **	—	1.9	2.1	2.8	3.6	4.3
			1.0	1.0	1.6	1.8	2.1
	Hg	1.0	1.6	3.1	5.7	9.0	—
		0.9	1.5	3.0	4.0	7.8	—
	Bi	—	0.03	0.09	0.13	0.16	0.18
			0.02	0.05	0.05	0.08	0.09
$10^{-8}W_{31}$, mol^{-1} s^{-1}	Ga **	—	0.4	1.3	1.9	3.3	5.2
			0.1	0.25	0.45	0.9	2.0
	Hg	0.30	0.75	1.4	3.4	8.0	—
		0.16	0.48	0.9	2.0	5.5	
	Bi	—	0.06	0.11	0.16	0.30	0.54
			0.03	0.05	0.07	0.15	0.27

* The upper row refers to H atoms, and the lower row to D atoms [$D^+(aq)$ ions in D_2O].
** Liquid electrode at 38 °C.

Ammonium ions are stronger PD than water molecules. The rate constants of electrochemical desorption involving them

$$H_{ads} + NH_4^+ + e^- \rightarrow H_2 + NH_3 \qquad (37)$$

on mercury are ~50 times greater than those for reaction (33) for identical values of $\gamma \simeq 0.18$ eV.

The ratio W_{31}/W_{30} increases with increase in $-E$ (Table 3), so that at low overvoltages, reaction (33) becomes the main reaction.

The electron transfer coefficient in electrochemical desorption from a polycrystalline gold electrode at $E \geqslant -0.1$ V increases to ~0.5,[32] that is there is a change from the activationless reaction to the normal reaction described by Eqn. (19), in accordance with the general ideas of the theory of electrode reactions.[28]

By comparing the values of W_3 measured by the LPE method with the ELH current

$$j_0 = 2ex_1N_{H^+}W_3/(W_2 + W_3), \qquad (38)$$

it is possible to find the surface concentration of H_{ads}:

$$\Gamma_H = j_0/2eW_3. \qquad (39)$$

Eqn. (39) follows directly from the quasi-stationary character of the ELH current, and is not based on any model considerations. The calculated $\Gamma_H(E)$ relationships are given in Fig. 8. The values

of Γ_H depend little on N_{H^+}, since W_3, like j_0, is proportional to N_{H^+}, when $W_{31}N_{H^+} > W_{30}$. The increase in Γ_H on going from Hg to Ga and Bi is due to the increase in κ_1, and the fact that the values of Γ_H are higher on Bi than on Ga is due to the decrease in W_3. The value of Γ_H does not exceed 3×10^{12} cm^{-2} on all three metals, and is small for measurements by the usual electrochemical methods.

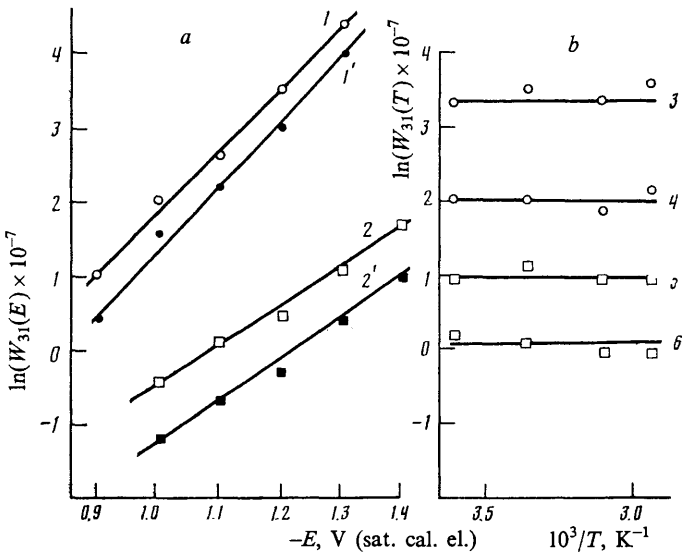


Figure 7. Dependence of the rate constant of the electrochemical desorption of hydrogen according to reaction (34) on the electrode potential (*a*) in H_2O (straight lines *1* and *2*) and D_2O (*1'*, *2'*) and on temperature (*b*) (straight lines *3*–*6*) on mercury (*1*, *1'*, *3*, *4*) and bismuth (*2*, *2'*, *5*, *6*) electrodes; the $W_{31}(E)$ relationships were measured at 22 °C, and $W_{31}(T)$ at $-E$ = 1.2, 1.0, 1.3, and 1.1 V (straight lines *3*–*6* respectively).[34]

The rate constants for the ionisation of H_{ads} on Hg were first measured by Benderskii and co-workers.[39,40] The $W_2(E)$ relationship is given in Fig. 9. In the range of E values from −0.6 V to −0.2 V, W_2 increases from 10^5 s^{-1} to 2×10^7 s^{-1} (β = 0.4–0.5), and in the range from −0.2 V to −0.1 V the transfer coefficient β decreases to 0.05–0.1. The decrease in β means that close to the equilibrium potential of ELH, the transfer coefficient for the direct reaction of hydrogen ion discharge (31) increases, tending to $\alpha_1 \simeq 1.0$, that is the Tafel law ($\alpha_1 = 0.50 \pm 0.05$), applicable for ELF at high overvoltages,[29,41] breaks down, and reaction (31) becomes barrierless. The suggestion that there is no barrier to the discharge of hydrogen ions at low overvoltages was previously put forward[42] (see also the book by Krishtalik[28]) on the basis of the fact that the overvoltage is independent of the composition of concentrated solutions of the anions adsorbed, although the data obtained,[42] like those in subsequent studies,[30,31] did not exclude a change not to barrier-free discharge but to quasi-equilibrium ($W_2 \gg W_3$) discharge, when it follows from Eqn. (38) that the effective transfer coefficient also becomes equal to 1. The results obtained by Babenko and co-workers[40] provide direct experimental confirmation of the existence of the barrier-free electrode processes assumed by Krishtalik.[42]

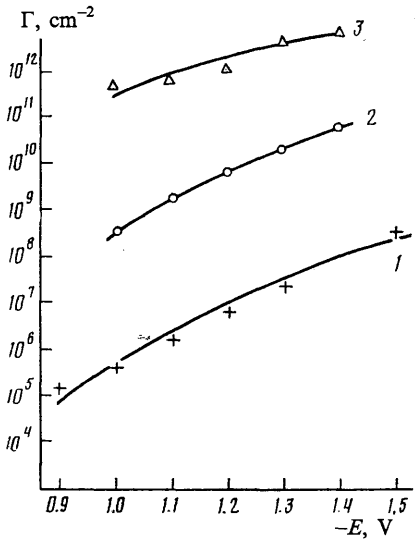


Figure 8. Surface concentration of hydrogen atoms adsorbed on mercury (*1*), liquid gallium (*2*), and bismuth (*3*).[36]

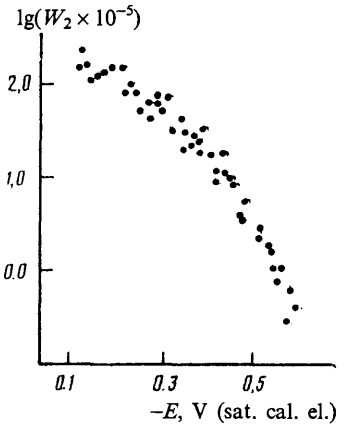


Figure 9. Dependene of the rate constant of the ionisation of hydrogen, adsorbed on mercury, on the electrode potential (0.3 M aqueous NaF solution with the addition of 0.01–0.03 M HF).[40]

As a result of the change in the transfer coefficients, the ELH exchange current on mercury is ~150 times smaller than that calculated by extrapolating the Tafel law to zero overvoltage (3×10^{-15} A cm^{-2} instead of 4×10^{-13} A cm^{-2}). A decrease in β analogous to that observed[40] for the mercury electrode was also observed on Au.[32] According to the detailed equilibrium principle,

the rate constants of reactions (31) and (32) are related by the thermodynamic expression

$$\frac{\kappa_1(E)}{W_2(E)} = \frac{\Gamma_H^0}{N_{H^+}^0} \exp\left(\frac{\Delta G(E)}{RT}\right), \quad (40)$$

where ΔG is the free energy of the discharge of $H^+(aq)$, and the values of Γ_H^0 and $N_{H^+}^0$ relate to the standard states. Eqn. (40) and the measured values of W_2 and j_0 can be used to find ΔG. When $\Gamma_H^0 = 10^{15}$ cm^{-2} (degree of coverage 1/2) is taken as standard state, the standard free energy ΔG^0 is 99.4 ± 3 kJ mol^{-1} (1.03 ± 0.03 eV). This agrees with the value found[42] from the temperature dependence of the barrier-free discharge current. The free energy of the adsorption of H atoms on mercury, equal to $\Delta G_H^0 - \Delta G$, is −104.1 ± 3 kJ mol^{-1}. The entropy of H_{ads}, according to an estimate[39] from the frequencies of the vibrations of the H atoms on the surface, does not exceed 8 J mol^{-1} K^{-1}, so that the energy of the Hg−H bond in the adsorbed state ($E_H = -\Delta G_a - T\Delta S_a$) is 136 ± 6 kJ mol^{-1}, confirming Frumkin's estimate of this quantity.[43]

Table 4. Values of E^0 and E^* for the two-electron stages of the electrochemical carbon cycle.[50]

Stage	pH	E^0, V (NHE)	E^*, V (NHE)
I. $CO_2+2e^-+2H^+ \rightarrow H_2CO_2$	0	−0.19	−0.73*
	3	−0.36	−1.04
	4.7	−0.43	−1.23
	7.0	−0.47	−1.23
II. $H_2CO_2+2e^-+2H^+ \rightarrow H_2CO+H_2O$	0	−0.01	−0.99*
	2.5	−0.15	−1.16
	3.5	−0.21	−1.23
	7.0	−0.58	−1.27
III. $H_2CO+2e^-+2H^+ \rightarrow CH_3OH$	0	0.24	−0.97*
	3.5	0.04	−1.06
	5.0	−0.06	−1.11
	7.0	−0.17	−1.17
IV. $CH_3OH+2e^-+2H^+ \rightarrow CH_4+H_2O$	0	0.58	−0.87*
	7.0	0.17	−0.87

*Obtained by extrapolating the E^* (pH) relationships.

The facts that α_1 is constant over a large range of change in κ_1, which for ELH reactions on mercury reaches 10^{12}, and that α_1 increases from 0.5 to 1.0 at low overvoltages, have been explained quantitatively using a theoretical model developed by Benderskii and co-workers.[29,44–46] In this model, the view that there is a reorganisation of the polar medium on electron transfer is supplemented by taking account of the simultaneous quantum displacement of the proton.[47,48] Allowance for the inter-related movement of the proton and the medium leads to the following expression for the rate constant of hydrogen ion discharge:

$$\kappa_1 = \kappa_1^0 N_{H^+} \exp\left(-\frac{(E_s + E_p + \Delta G^0 - e(E_H^0 - E))^2}{4E_s kT + F^2\delta^2}\right), \quad (41)$$

where E_s and E_p are the energies of reorganisation along the coordinates of the medium and the proton respectively; δ the amplitude of the zero-point vibrations of the proton in the initial state; F the curvature of the proton term of the final state M−H; E_H^0 the potential of the normal hydrogen electrode (NHE); and κ_1^0 a pre-exponential term determined by the rate of tunnel electron transfer. According to Eqn. (41), the Tafel law applies for

$$e(E_H^0 - E) < E_s + E_p + \Delta G^0, \quad (42)$$

that is the reason for its applicability over a wide range of E is the high total energy (~3.3 eV, as shown below) of the reorganisation (the intramolecular reorganisation and that of the environment of the reaction complex).

The discharge becomes barrier-free when[46]

$$\Delta G^0 > E_s\left(1 - \frac{4kT}{\hbar\omega}\right) + e(E_H^0 - E), \quad (43)$$

where ω is the frequency of the vibrations of the proton in the initial state. The theoretical model describes the change in $\kappa_1(E)$ in the range of both normal and barrier-free discharge, where the value of κ may change by a factor of more than 10^{18}. The values of E_s and E_p are 1.75 eV and 1.55 eV respectively. Thus the LPE method, which makes it possible for the first time to measure the absolute values of the rate constants of rapid ELH reactions, has led to the development of existing ideas on the mechanism of one of the most fundamental electrochemical processes.

VII. Intermediate species of the electrochemical carbon cycle

The electrochemical reduction of carbon dioxide to methane (the electrochemical carbon cycle) is an eight-electron process in which stable products: formic acid, formaldehyde, methanol, and methane, are formed at each of the successive two-electron stages. The redox potentials of these stages are given in Table 4. In acidic and neutral solutions in the absence of overvoltage, all the stages of the carbon cycle should have an appreciable rate even in the region of E_H^0. The overvoltage of stages (I) and (III), however, is greater than 1 V, and the reduction of H_2CO_2 and CH_3OH in aqueous solutions requires even higher overvoltages.[49] As in ELH reactions, the overvoltage is due to the formation of high-energy IS. An important role in the study of their electrochemistry was played by work[2,3,50–52] carried out by the PECR method, which established that for the radicals of the carbon cycle CHO, CH_2OH, and CH_3 there exists a fairly wide range of potentials in which the rate constants of the oxidation and reduction are lower than 10^3 s^{-1}. The relative electrochemical stability of the radicals and the weak pH dependence of the potentials of the polarographic waves of CH_3 and CH_2OH indicated that the products of the electrode reactions of the radicals are the high-energy organic ions CHO^-, CH_2OH^-, and CH_3^-, which then undergo homogeneous transformations into stable products (CH_2O, CH_3OH, and CH_4 respectively), whereas the exothermic electron−proton transfer reactions

$$R + e^- + H^+(aq) \rightarrow RH \quad (44)$$

take place at very low rates. The formation of CH_3^-, and not CH_4, in the reduction of CH_3 has been confirmed.[53] Calculation of the free energy of reactions (44) [2,54] also shows that the formation of HCO and CH_3 radicals cannot be responsible for the high overvoltage of stages (II) and (IV), that is the mechanism of the reactions of the carbon cycle is much more complex than a simple sequence of one-electron stages involving the formation and reduction of radicals. Low rates of reactions (44) have also been observed for many homogeneous processes associated with the formation of a CH bond with proton transfer.[55]

Each of the two-electron stages of the carbon cycle can be represented by the scheme

$$A \underset{W_2}{\overset{W_1}{\rightleftharpoons}} R \underset{W_4}{\overset{W_3}{\rightleftharpoons}} B, \tag{45}$$

which leads directly to the relationship between E^* and the standard potential B/A:

$$E^* = E^0 - \frac{kT}{e(\alpha+\beta)} \ln \frac{W_2^0}{W_3^0}, \tag{46}$$

where the rate constants of the electrode reactions of the radical W_2^0 and W_3^0 refer to the potential E^0 at which the two channels for the transformation of R have the same free energy. Since the rates of the transformation of the same species by two channels of equal energy under identical conditions cannot differ greatly, E^* and E^0 should be approximately equal. Thus by comparing the values of E^* and E^0 for the stages of the carbon cycle it is possible to establish whether the stable species listed in Table 4 are the products of the electrode reactions of the radicals.

The rate constants of the electrode reactions of the radical ion CO_2^- have been measured by the LPE method.[56,57] The $W_2(E)$ and $W_3(E)$ relationships are given in Fig. 10. The fact that the kinetic curves $Q(t)$ are exponential indicates that the electrode reactions involve adsorbed IS. Oxidation is observed at $E > -1.4$ V, W_2 is independent of pH and is equal to 3.5×10^6 s^{-1} at -1.35 V, and $\beta = 0.55-0.65$. Reduction takes place at $E < -1.5$ V, and $\alpha = 0.25-0.30$. The value of W_3 is linearly dependent on N_{H^+}. The participation of hydrogen ions in the reduction is confirmed by the marked isotope effect; the value of W_3 in H_2O solutions is three times that in D_2O. There is no isotope effect in the oxidation. The pH dependence of E^* is described by Eqns. (35) and (46);

for $W_{31}N_{H^+} \gg W_{30}$, the derivatives of $\frac{dE^*}{d\,pH} = -\frac{2.3}{\alpha+\beta}\frac{kT}{e}$,

and for $W_{31}N_{H^+} < W_{30}$ (pH $\geqslant$ 4.5), the potential E^* is constant. The polarograms obtained[53,56,57] for the CO_2^- ion generated by a low-frequency photo-emission current ($\Omega \ll W_2 + W_3$) give the sum of the transfer coefficients, which correspond to the values found by the pulse method.

According to Buxton and Sellers,[58] pK for the carboxyl radical HCO_2 is 1.4, so that in the solutions with pH $\geqslant$ 2.5 in which the LPE was measured, the IS are present as the radical ion CO_2^-. On adsorption on a negatively charged metal surface, the IS is apparently converted into the protonated form. The electrode reactions take place according to the equations:

$$HCO_2 \xrightarrow{W_2} CO_2 + H^+ + e^-,$$

$$HCO_2 + e^- + H^+ \xrightarrow{W_3} H_2CO_2. \tag{47}$$

At pH $\geqslant$ 4.5, water molecules become the main proton donors. From the numerical values of the constants found by the LPE method, it follows that in the region of E^* there is a change from the quasi-equilibrium reduction of CO_2 ($E > E^*$, $W_2 > W_3$) to ordinary reduction, and this change, in accordance with Eqn. (38), is in fact accompanied by a decrease in the effective transfer coefficient from $1 + \alpha$ to $1 - \beta$.[59] The measured[59] polarisation dependence of the current of the two-electron reduction of CO_2 coincides with the curves calculated from the LPE data using Eqn. (38). This means that the oxidation product of HCO_2 is CO_2. Comparison of the reduction current of CO_2, that is the values of κ_1, with W_2 made it possible, using Eqn. (40), to find the standard free energy of the reaction

$$CO_2 + e^- + H^+(aq) \rightarrow HCO_{2\,ads}, \tag{48}$$

equal to $\sim$154 kJ mol^{-1}. The coverage of the mercury surface by the radical does not exceed 10^8 particles cm^{-2}.

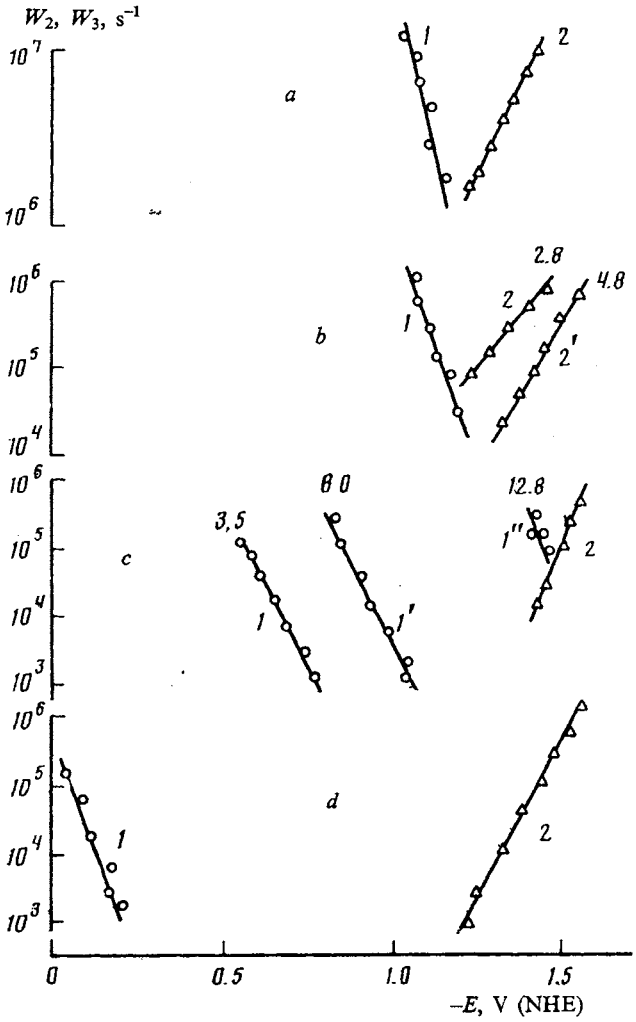


Figure 10. Tafel relationships for the rate constants of the oxidation (*1*, *1'*, *1''*) and reduction (*2*, *2'*) of the radicals CO_2^- (*a*), HCO (*b*), CH_2OH (*c*), and CH_3 (*d*) of the electrochemical carbon cycle at a mercury electrode; the pH values are given at the straight lines; for the other reactions, W_2 and W_3 are independent of pH.[54]

The electrode reactions of formyl radicals adsorbed on mercury have been studied.[60] As in the case of HCO_2, the rate constant for the oxidation of HCO [or its hydrated form $HC(OH)_2$] is independent of pH, and W_3 increases with decrease in pH, indicating that the reduction of the radical involves one hydrogen ion.

The values of W_2 and W_3 (Fig. 10) change from 10^4 s^{-1} (at $-E$ = 1.3–1.5 V) to 10^6 s^{-1} (at $-E$ = 1.5×1.8 V) (β = 0.45, α = 0.27). E^* changes in accordance with the pH dependence of W_3 (Table 4). At pH ⩾ 4, the reduction involves water molecules, leading to a change in the transfer coefficient (α' = 0.35).

The difference $E^0 - E^*$ for the carboxyl and formyl radicals (Table 4) is such that it corresponds to a difference in W_2^0 and W_3^0 in Eqn. (46) by $10^{10}-10^{15}$. The unrealistic value of this difference indicates that the reduction of these radicals involves the formation of products with much higher energies than formic acid and formaldehyde. The fact that the reduction involves one electron and one proton shows that these species with higher energy must be isomers of these stable compounds. A high-energy isomer of formaldehyde is hydroxymethylene HCOH, formed, in particular, by the recombination of HCO and H after the photodissociation of H_2CO.[61] According to published data,[61,62] the energy of the ground state of HCOH is ~2.2 eV greater than that for H_2CO, so that the value of E^0 for the reaction

$$H_2CO_2 + 2H^+ + 2e^- \rightarrow HCOH + H_2O \qquad (49)$$

is close to –1.1 V and corresponds to the measured values of E^*. By analogy with the formyl radical, the product of the one-electron reduction of HCO_2 is apparently dihydroxymethylene $C(OH)_2$ [or its anion $C(OH)O^-$ in the reduction of CO_2^-]. These carbene derivatives subsequently undergo homogeneous isomerisation to H_2CO and H_2CO_2. Judging from a quantum-chemical calculation,[61] the barrier to the intramolecular rearrangement of *cis*-hydroxymethylene into H_2CO is ~50 kJ mol^{-1}, and the lifetime of HCOH in the gas phase is 4 μs.[63] The formation of carbene derivatives in electron–proton transfer reactions is consistent with the existing view that the hydrogen atom adds on to oxygen much more readily than to carbon.[55]

The methanol radical[64–66] is electrochemically much less active than HCO_2 and HCO; the constants W_2 and W_3 are 10^2-10^5 s^{-1} (Fig. 10). The rate constant for the reduction of CH_2OH adsorbed on mercury is independent of pH in the range 3–13, and remains unchanged when 1 M NH_4^+ ions as PD are added to the solution. The transfer coefficient for W_3 is 0.68. Unlike W_3, the rate of oxidation increases sharply with increase in pH, and change in pH also leads to a change in the transfer coefficient. In the pH range 3.5–7, β = 0.63, and the displacement of E with change in pH at constant W_2 (dE/dpH) is ~0.06 V. In the pH range 8–12, β = 0.3, and dE/dpH ≃ 0.16, corresponding to a first order reaction with respect to OH^- ions. At pH ⩾ 12.5, at which the radical is present in the ionic form (pK = 10.6[3]), W_2 is independent of pH, and β = 0.5. The dependence of W_2 and W_3 on pH and E corresponds to the reactions

$$CH_2OH + OH^- \rightarrow CH_2O + H_2O + e^-,$$
$$CH_2OH + e^- \rightarrow CH_2OH^-. \qquad (50)$$

At pH ⩽ 8, water molecules act as hydrogen acceptors in the oxidation of the radical. Because of the relatively low values of W_2 and W_3, the surface concentration of the radical increases to such an extent that its electrode reactions can be detected by ordinary electrochemical methods, in particular by the cyclic voltammetric study of formaldehyde solutions. The $\Gamma(E)$ relationships calculated using Eqn. (39) from the polarisation curves for the reduction of H_2CO[49] are given in Fig. 11. They agree with published data;[49,67,68] appreciable accumulation of the radical is observed in the pH range 6.8–9.0, and is not recorded in more alkaline solutions. The position and height of the maxima of the anodic current on the voltammetric curves[67,68] coincide with those calculated from the measured[66] constants W_2 and W_3. The published[66] comparison of the LPE and cyclic voltammetric data shows that the IS generated in photo-emission and in the reduction of CH_2O are identical. In both cases the IS is CH_2OH. The fact that W_3 is independent of pH, indicating that hydrogen ions do not take part in the reaction, the high transfer coefficient, characteristic of endothermic reactions, and the large difference in the potentials E^* and E^0 for the formation of CH_3OH from CH_2O (Table 4) show that the reduction product of formaldehyde is the carbanion CH_2OH^-, and not methanol. The calculated[69] energy of the tautomerisation of the methoxide ion CH_3O^- into CH_2OH^- is ~93 kJ mol^{-1}. The potential E^0 for the reaction

$$CH_2O + 2e^- + H^+ \rightarrow CH_2OH^-(aq), \qquad (51)$$

calculated from this value and pK for CH_3OH, agrees with the measured value of E^*. The free energy of the adsorption of CH_2OH on mercury is –40 kJ mol^{-1},[66] and for HCO_2, ΔG_a = –44 kJ mol^{-1}.[56]

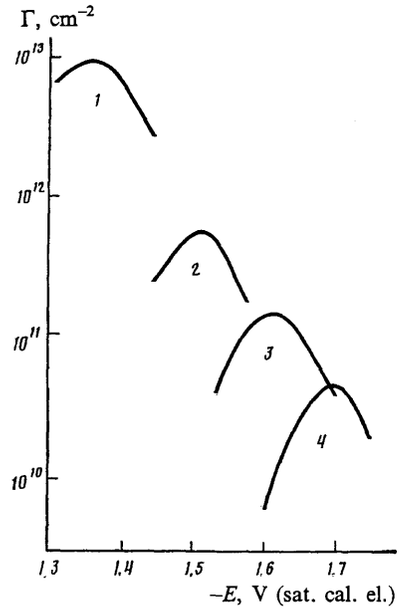


Figure 11. Surface concentration of the CH_2OH radical in the reduction of formaldehyde at a mercury electrode at different pH values: *1*, 6.8; *2*, 9.0; *3*, 11.1; *4*, 13.0.[66]

The reduction of CH_3 also takes place without the participation of PD, and leads to the formation of the CH_3^- anion, whose free energy has been calculated.[3]

The diagram of the free energies of the successive one-electron reactions of the electrochemical carbon cycle, based on the values of E^* given in Table 4 for stages (I)–(III) and the thermodynamic characteristics of the free radicals,[70] is given in Fig. 12. In a neutral

solution, the free energy of the overall process

$$CO_2 + 8\,H_2O + 8\,e^- \rightarrow CH_4 + 8\,OH^- \qquad (52)$$

is 204 kJ mol^{-1}. The additional energy losses at each of the two-electron stages are due to the transformation of the reduction products of the radicals $C(OH)_2$, HCOH, CH_2OH^-, and CH_3^- into H_2CO_2, H_2CO, CH_3OH, and CH_4 respectively, and amount to 755 kJ mol^{-1}. From this it follows that the energetic efficiency of the electrochemical carbon cycle does not exceed 21%. Since the energy losses are due to the formation of the carbanions CH_2OH^- and CH_3^-, which are not adsorbed on the negatively charged electrode surface, the efficiency of the corresponding stages is the same for different metals. Thus even the energy efficiency (without allowance for current losses) of the sequence of one-electron reactions being considered is extremely low, so that it is important to find catalytic electrochemical systems in which either two-electron transfer without the intermediate formation of radicals or simultaneous electron transfer and proton addition with the formation of a CH bond are possible.

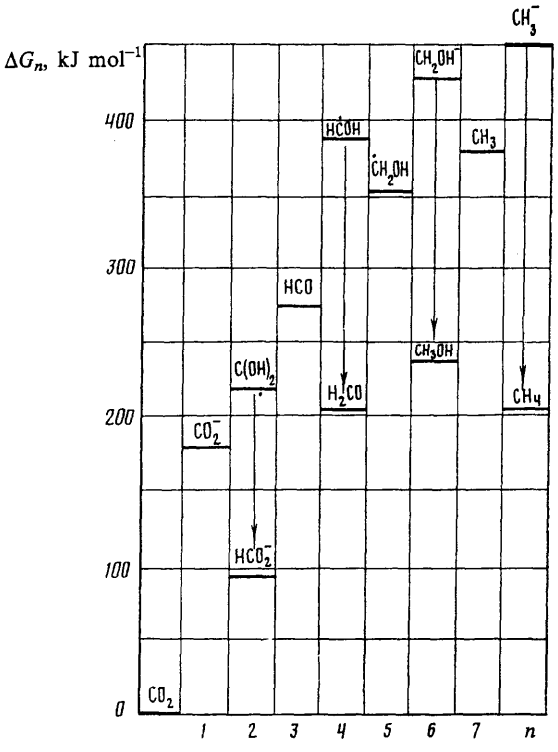


Figure 12. Free energies of the reactions of the electrochemical carbon cycle at pH 7.

VIII. Electrochemistry of alkyl and hydroxyalkyl radicals

Alkyl radicals are IS in the two-electron reduction of alkyl halides;[71] they are also formed in the one-electron reduction of alkylmercury compounds.[72,73] The PECR method gave the polarograms of CH_3 at a mercury electrode 10^{-5} s after a radiolysis pulse, and detected a wide range of potentials in which the CH_3 radical is electrochemically inactive.[2] It has been suggested that the reduction product of CH_3 is the carbanion CH_3^-, and not methane.[2,53,72,73] The rate constants of the electrode reactions of alkyl radicals could not be measured by electrochemical methods, since their recombination is a multi-stage process. It has been suggested[72,74] that the formation of HgR_2 is preceded by the rapid formation of the organic calomel Hg_2R_2, capable of dissociation, and that the radicals are present on the mercury surface as HgR. The rate constants of the heterogeneous reactions of these radicals have been measured by the LPE method.[24] In the working range of the mercury electrode ($E < -0.1$ V), only the oxidation of CH_3 is observed. The Tafel straight lines $\ln W_3(E)$ are displaced to more negative values of E in the series CH_3, C_2H_5, n-C_3H_7, n-C_4H_9. There exists a wide range of E (for CH_3, for example, from -0.6 V to -1.3 V) in which there are no IS electrode reaction currents, that is the rates of these reactions are lower than the rate of surface recombination. An analysis of the polarograms recorded at different Ω gave the rate constants of the last process, which takes place according to the scheme

$$\begin{array}{ccccc} CH_3Hg^+ & \overset{W_2}{\leftarrow} & CH_3Hg & \overset{W_3}{\rightarrow} & CH_3^- + Hg^+ \\ & \gamma\downarrow & \uparrow k_2 & & \\ & & (CH_3)_2Hg_2 & \overset{k_3}{\rightarrow} & (CH_3)_2Hg \end{array} \qquad (53)$$

with $\gamma = 5 \times 10^{-9}$ cm^2 s^{-1}, $k_2 = 3 \times 10^2$ s^{-1}, $k_3 \simeq 20$ s^{-1}. The values of the constants correspond to the cyclic voltammetric curves for the radical.[73] The surface concentrations of the radical (Γ_R) and the dimer (Γ_d) in the kinetic scheme (53) are:

$$\Gamma_R = \frac{W}{2m\gamma}\left(\sqrt{1+\frac{4mj_R}{W^2}}-1\right), \quad \Gamma_d = \frac{m\gamma}{k_3}\Gamma_R^2, \quad m = \frac{k_3}{k_2+k_3}, \qquad (54)$$

where j_R is the current of the electrochemical or photo-emission formation of CH_3. In the range in which the radical is electrochemically stable ($W < \gamma\Gamma_R$), the adsorbate exists chiefly as the dimer ($\Gamma_d \gg \Gamma_R$). When the rate of the electrode reactions increases to such an extent that $W > \gamma\Gamma_R$, the concentrations Γ_R and Γ_d decrease, and $\Gamma_R > \Gamma_d$. During the cyclic scanning of the potential in the range corresponding to the reduction of RHg^+, the dimer accumulates, and the limiting stage of the reduction at $E \leqslant -1.3$ V becomes its decomposition to radicals with rate constant k_2.

According to PECR data,[50,75] the α-ethanol radical CH_3CHOH, which is an IS in the reduction of acetaldehyde, is oxidised with a rate constant W_2 which decreases from 10^5 s^{-1} to 10^4 s^{-1} in the range of E values from -1.0 V to -1.3 V. The $W_2(E)$ and $W_3(E)$ relationships for this radical, measured by the LPE method,[21,76] are similar to the corresponding relationships for the CH_2OH radical (see Fig. 10). The reduction rate constant W_3 is independent of pH. The $W_3(E)$ relationships measured in the range $10-10^3$ s^{-1} and 10^4-10^5 s^{-1},[75,76] lie on the same Tafel straight line, and in this case the transfer coefficient α is 0.5. The constant W_2 increases with pH at pH > 8, in agreement with the fact that the oxidation is first order with respect to OH^- ions [see Eqn. (50)]. At pH < 7, the constant W_2 is independent of the acidity, that is the radical is oxidised to the aldehyde with the formation of a hydrogen ion.

The $W_2(E)$ and $W_3(E)$ relationships for the isopropyl alcohol radical at different pH values (Fig. 13) show that the oxidation and reduction of this radical take place by the same mechanism as the transformations of CH_2OH and CH_3CHOH. Studies of the electrochemical reduction of acetone[77,78] have shown that the adsorbed radical $(CH_3)_2COH$ is the IS in this process.

At $E > -1.3$ V, the formation of the radical in acidic solutions takes place in quasi-equilibrium fashion ($W_2 > W_3$), so that under the conditions of a cyclic increase in E, the IS is oxidised almost quantitatively to acetone. The absolute values of W_2, measured by the potential jump method,[77] increase from 10^4 s^{-1} to 4×10^4 s^{-1} with increase in E from –1.3 V to –1.23 V ($\beta = 0.5$). The formation of the radical in the reduction of acetone is a first-order reaction with respect to hydrogen ions. The order of magnitude of the values of W_2 measured by the LPE method agrees with that of published data;[77] the β values also coincide. A quantitative comparison of the results obtained by these two methods is difficult, because of the difference in the pH and acetone concentrations at which the measurements were carried out (pH < 1 and $N_a \simeq 4$ M in the study of Brown and Lister,[77] and pH $\geqslant$ 4 and $N_a \leqslant 0.5$ M in the LPE measurements). Since acetone and the radical are adsorbed on mercury, the values of W_2 correspond to different degrees of coverage of the surface. The values of W_3 measured by LPE and low-frequency photoemission methods[21,64] at pH $\geqslant$ 4 are smaller by factors of 10^3-10^4 than those corresponding to the current for the reduction of acetone to isopropyl alcohol at pH $\leqslant$ 1.[77] This difference indicates that in strongly acidic solutions, the reduction of the radicals involves hydrogen ions:

$$(CH_3)_2COH + e^- + H^+ \rightarrow (CH_3)_2CHOH, \quad (55)$$

whereas at pH $\geqslant$ 4, as in the case of CH_2OH and CH_3CHOH, the reduction product is the carbanion $(CH_3)_2COH^-$. With two parallel channels for the quasi-equilibrium formation of the radical, the reduction current of acetone is given by the relationship

$$j_0 = 2e\Gamma_0 \frac{W_1}{W_2} N_{H^+}(W_{30} + W_{31}N_{H^+}), \quad (56)$$

where Γ_0 is the surface concentration of acetone, and W_1 the rate constant for its reduction to the radical, equal to 3×10^2 s^{-1} at $E = -1.28$ V in 0.5 M H_2SO_4 solution ($\alpha_1 = 0.5$).[77] It follows from Eqn. (56) that $j_0 \sim N_{H^+}^2$ when $W_{31}N_{H^+} > W_{30}$, in agreement with published data.[78] Comparison of the values of W_{30} and W_{31} measured by the LPE and potential jump methods shows that at pH 3, $W_{31}N_{H^+} \simeq W_{30}$. In alkaline solutions, the main reduction product of acetone is pinacone, which, as suggested as early as 1927,[79] is formed either by the bimolecular recombinations of the radicals or by the reaction of acetone with the carbanion. With increase in pH, the rate constant W_2 increases, and the reduction of acetone takes place at more negative potentials, at which, as a result of the increase in W_3, the concentration of the radical decreases [see Eqn. (39)], as in the case of the methanol radical (see Fig. 10). The decrease in Γ with increase in pH does not agree with the first of these mechanisms, whereas with increase in W_3, which indicates an increase in the rate of formation of the carbanions, it is possible to explain the increase in the yield of pinacone in alkaline solutions.

According to PECR [2,3] and LPE data, the reduction of the β-ethanol radical CH_2CH_2OH involves one hydrogen ion:

$$CH_2CH_2OH + e^- + H^+ \rightarrow C_2H_4 + H_2O. \quad (57)$$

The values of W_3 change from 10 s^{-1} to 10^5 s^{-1} in the range of E values from –0.65 V to –1.34 V at pH 5.5 ($\alpha \simeq 0.4$). The marked displacement of the reduction potential of the radical into the cathodic range compared with the expected potential for the production of ethylene according to Eqn. (57), for which the free energy is –131 kJ mol^{-1}, indicates that the reaction product is the adsorbed biradical CH_2-CH_2. This is consistent with the high overvoltage observed in the electrochemical synthesis of cycloalkanes from their dihalogeno-derivatives,[71] taking place at $E \leqslant -2.0$ V.

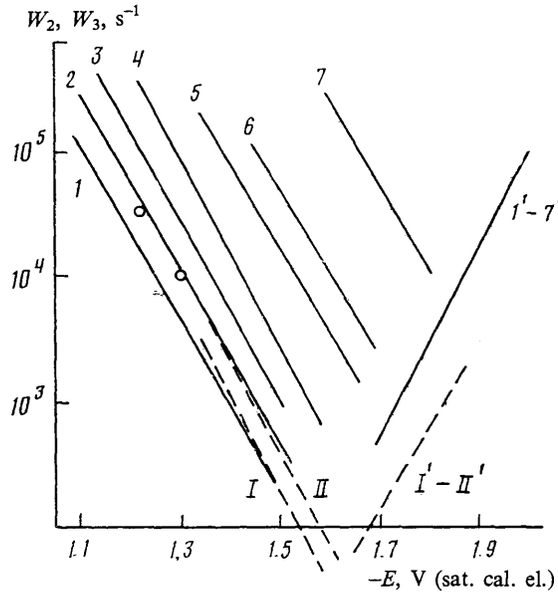


Figure 13. Tafel relationships for the rate constants of the oxidation (*1*–*7*) and reduction (*1'*–*7'*) of the isopropyl alcohol radical adsorbed on a mercury electrode at different pH values: *1*, *1'*, pH 4.25; *2*, *2'*, pH 6.8; *3*, *3'*, pH 7.35; *4*, *4'*, pH 8.1; *5*, *5'*, pH 9.15; *6*, *6'*, pH 10.0; *7*, *7'*, pH 10.8; the points give the values measured by Brown and Lister,[77] and the broken lines the data of Rotenberg and Rufman;[64] the straight lines *I* and *I'* were obtained at pH 4.6, and *II* and *II'* at pH 7.0.

Mairanovskii[80] has suggested that there is no protonation with the formation of a CH bond in the electrode reactions of organic compounds. The opposite view was put forward by Elving,[81] who considered that the reduction of organic compounds is analogous to the electrochemical desorption of hydrogen.

The above data obtained by the LPE method, which has made it possible for the first time to measure systematically the rate constants of the electrode reactions of simple alkyl and hydroxyalkyl radicals, provide clear evidence in support of the first suggestion. Even in the reduction of the $(CH_3)_2COH$ radical in acidic solutions, where it was possible to observe the electron–proton transfer reaction (55), its rate constant was 10^6 times smaller than the rate constant for electrochemical desorption (Table 3). For other radicals, W_{31} is even smaller. The diagram in Fig. 12 makes it possible to estimate quantitatively the difficulty of protonation with the formation of a CH bond. For example, the exothermic formation of methane from the methyl radical takes place at a lower rate than the endothermic formation of the CH_3^- ion, although ~180 kJ mol^{-1} is liberated in the first reaction, whereas 75 kJ mol^{-1} is used up in the second. The CH_2OH^- and CH_3CHOH^- anions are formed instead of methane and ethanol, despite the fact that the free

energies of formation of these carbanions from the radicals are ~170 kJ mol^{-1} greater than those for the alcohols. Thus the barrier associated with the reorganisation of the the complex in the transfer of a proton with the formation of a CH bond for simple organic radicals is greater than 150–200 kJ mol^{-1}. Since the rates of protonation with the formation of an OH bond are much higher, carbene derivatives are formed in the reduction of carboxyl radicals.

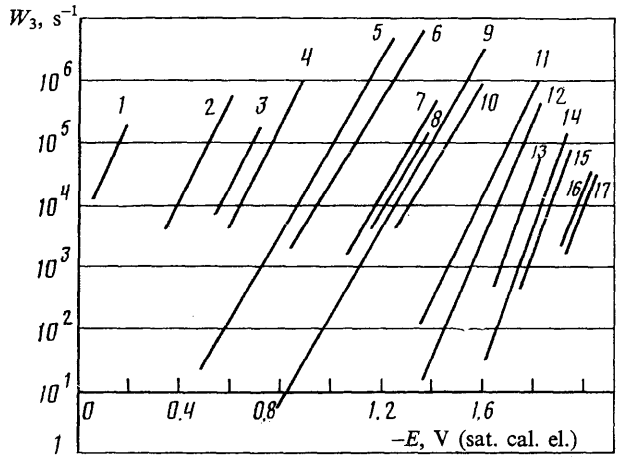


Figure 14. Tafel relationships for the rate constants of the reduction of simple organic radicals to carbanions:[82] *1*, CCl_3; *2*, CCl_2F; 3, $CClF_2$; *4*, CF_3; *5*, $CHCl_2$; *6*, CHFCl; *7*, CHF_2; *8*, C_6Cl_5; 9, CH_2Cl; *10*, C_6H_5; *11*, CH_3; *12*, CH_2OH; *13*, C_2H_5; 14, C_2H_4OH; *15*, $(CH_3)_2COH$; *16*, n-C_3H_7; *17*, n-C_4H_9.

IX. The p*K* scale for weak CH-acids

The rate constants for the one-electron reduction of a number of simple organic radicals to carbanions have been measured by the LPE method.[82] The $W_3(E)$ relationships for all the radicals studied have similar values of the transfer coefficient $\alpha = 0.45 \pm 0.05$ (Fig. 14). An empirical rule was proposed[82] for relating the potentials of the Tafel straight lines $\ln W_3(E)$ to the energy characteristics of the carbanions: the displacement of the standard redox potential E^0 of the reaction

$$R + e^- \rightarrow R^- \qquad (58)$$

for a series of organic radicals is equal to the displacement of the potential corresponding to identical values of W_3. The equation for the retarded discharge can be written as:

$$\ln W_3 = \ln W_3^0 - \frac{E_a^0}{RT} - \alpha\frac{\Delta G_a^0}{RT} + \alpha\frac{E}{RT}(E^0 - E), \qquad (59)$$

where E_a^0 and W_3^0 are respectively the activation energy and the pre-exponential term for $E = E^0$. In Eqn. (59), allowance has been made for the fact that the radical is present in the adsorbed state. It follows from Eqn. (59) that the relative displacement of the Tafel straight lines along the E scale for equal values of W_3 and α is related to the difference in E^0 by the expression

$$\Delta E_{12} = \Delta E_{12}^0 - \frac{RT}{\alpha F}\ln\frac{W_{31}^0}{W_{32}^0} - \frac{1}{\alpha F}(E_{a_1}^0 - E_{a2}^0) - \frac{1}{F}(\Delta G_{a1}^0 - \Delta G_{a2}^0). \qquad (60)$$

According to Eqn. (60), the rule formulated above ($\Delta E_{12} = \Delta E_{12}^0$) applies if the transfer coefficients of the radicals, the pre-exponential terms, the activation energies E_a^0, and the free energies of adsorption coincide. It has been established experimentally that α is constant. The fact that E_a^0 and W_3^0 coincide is a direct consequence of the model of electron transfer in a polar medium;[47,48] according to this model, W_3 characterises the probability of electron transfer from the metal to the reaction complex, and $E_a^0 = E_s/4$ (E_s is the energy of reorganisation of the medium in this transfer). The requirement that ΔG_a^0 be constant, which means the preservation of the energy of the M–C bond in the series of radicals, is the least rigid of the above conditions, since this quantity is comparatively small ($\leqslant 50$ kJ mol^{-1}).

From the empirical rule and the measured values of $W_3(E)$, it is possible to compile a scale of relative values of E^0. To change to the absolute scale, the standard potentials of the following reactions were calculated[82]

$CH_3(gas) + e^- \rightarrow CH_3^-(aq)$ and
$CH_2OH(gas) + e^- \rightarrow CH_2OH^-(aq)$:

$$E^0 = \frac{F}{RT}(\Delta G_{R^-}^0 - \Delta G_R^0) = \frac{F}{RT}(\Delta G_h^0 - EA - \Delta G_{H^+}^0 - RT\ln 24{,}5), \qquad (61)$$

where ΔG_h^0 is the hydration energy of R^-, EA the electron affinity of the radical in the gas phase, and $\Delta G_{H^+}^0 = -430$ kJ mol^{-1} the standard free energy of hydration of the proton, used to change from the energy scale in a vacuum to the energy scale in aqueous solution. The last term in Eqn. (61) takes account of the difference between the standard states of the ion in the gas and in solution. The value $\Delta G_h^0 = -322$ kJ mol^{-1} for CH_3^-, taken as equal to the hydration energy of the hydride ion,[2] is close to the values of ΔG_h^0 for the NH_4^+ and K^+ ions (−314 kJ mol^{-1} and −330 kJ mol^{-1} respectively), which have approximately the same dimensions. The electron affinity of the methyl radical is 7.7 ± 2.9 kJ mol^{-1},[83] so that the free energy of the CH_3^- ion in water is 230 ± 16 kJ mol^{-1} and $E^0 = -0.77 \pm 0.16$ V. The calculated energy of the ground state of the CH_2OH^- ion is 93 kJ mol^{-1} greater than the energy of CH_3O^-.[84] Using the value of pK (CH_3OH) and assuming that the solvation energies of the two ions are equal, it is found that for $CH_2OH^-(aq)$, $\Delta G^0 \simeq 60$ kJ mol^{-1}, and $E^0 = -0.85$ V. The difference in E^0 for these two reactions corresponds to the displacement of the Tafel curves. The free energies of the other carbanions are given by the expression

$$\Delta G_{R^-}^0 = \Delta G_{R_0^-}^R + \delta(\Delta G_{CH}^0) + \frac{RT}{F}\Delta E^0, \qquad (62)$$

where $\Delta G_{R_0^-}^0$ is the free energy of the "standard" carbanion CH_3^-, and $\delta(\Delta G_{CH}^0)$ the difference between the free energies of the rupture of the CH bond in R_0H and RH. In Eqn. (62), the difference in the hydration energies of R and RH is not taken into account. The free energies of different carbanions are given in Table 5, which also gives the values of E^0 and pK for the CH-acids conjugate with R^-:

$$pK = \frac{1}{2{,}3RT}(\Delta G_{R^-}^0 - \Delta G_{RH}^0), \text{ where } \Delta G_{RH}^0 \text{ is the free energy of RH.}$$

The pK scale defines the relative reactivity of organic substances in nucleophilic substitution reactions.[85] Several methods have been proposed for constructing it from indirect data, in particular from the rate constants of proton exchange.[86] Attempts have been made to determine the pK values by semi-empirical quantum-chemical calculations.[87] The most universal is the polarographic pK scale, constructed using the half-wave potentials for the two-electron

reduction of the symmetrical organomercury compounds HgR_2 to the carbanions in non-aqueous solvents.[88] It was assumed[88] that the reduction of HgR_2 takes place under conditions close to equilibrium, and that the change in $E_{1/2}$ corresponds to the displacement of pK. Because of the complexity of the two-electron process, indicated, for example, by the above data on the reduction of CH_3Hg^+ to CH_3^-, this approximation is less obvious than that used by Benderskii and co-workers.[82] The values of pK found by different methods sometimes differ by factors of $10^{10}-10^{12}$.[88] For comparison, it may be noted that even a difference by factors of 10^3-10^4 in the pre-exponential terms in Eqn. (60) leads to a scatter in the relative values of pK of 5–7 units. The pK values for the haloforms CHF_3 and $CHCl_3$ found by the published methods[88,82] coincide.

Table 5. Free energies of organic radicals (ΔG^0_R) and carbanions ($\Delta G^0_{R^-}$, aq), standard redox potentials E^0 of the formation of the carbanions from the radicals, and the pK values of CH-acids RH.[82]

Radical	ΔG^0_R, kJ mol^{-1}	ΔG^0_R, kJ mol^{-1}	$-E^0$, V	CH-Acid	pK
CH_3	145	(230)	(0.77)	CH_4	(47)
C_2H_5	139	247	0.95	C_2H_6	48.5
n-C_3H_7	148	263	1.18	**n-C_3H_8**	49.6
n-C_4H_9	160	276	1.19	**n-C_4H_{10}**	50.8
CH_2OH	—18	60	0.85	CH_3OH	40.8
CH_3CHOH	39	61	1.01	C_2H_5OH	42
$(CH_3)_2COH$	26	73	1.04	$(CH_3)_2CHOH$	42.7
CH_2Cl	122	176	0.42	CH_3Cl	39.5
$CHFCl$	—85	—49	0.12	CH_2FCl	31.7
CHF_2	—237	—203	0.36	CH_2F_2	37.3
$CHCl_2$	95	98.5	0.04	CH_2Cl_2	31.2
CF_2Cl	—269	—295	—0.26	CHF_2Cl	23.2
$CFCl_2$	82	—122	—0.44	$CHFCl_2$	19.9
CF_3	—456	—283	—0.18	CHF_3	29.7
CCl_3	95	19.1	—0.79	$CHCl_3$	15.2
C_6H_5	349	397	0.49	C_6H_6	46.2
C_6Cl_5	—	—	0.42	C_6HCl_5	38

The pK values for CH-acids in the gas phase have been found by measuring the electron affinity of the radicals by the ion-cyclotron resonance method.[89,90] Although these data are extremely convenient for determining the influence of different substituents on pK, they cannot be used to construct the pK scale for solutions, since the differences in the solvation energies of the carbanions mask the changes in acidity associated with the introduction of the substituents. For example, the pK values for the CH-acids CH_4 and CHF_3 differ by 29 units in the gas phase,[89] and by 17 units in aqueous solution, that is the difference ΔG^0_h is 69 kJ mol^{-1}.

The pK scale in solutions is not universal, since the change to another medium changes $\Delta G^0_{R^-}$ by an amount equal to the free energy of the transfer of the carbanion between the solvents ΔG^0_t. For inorganic ions, the value of ΔG^0_t lies in the range 10 to 25 kJ mol^{-1}.[91] In the method of Benderskii and co-workers,[82] change in the solvent leads to additional errors due to the relative changes in the energy of reorganisation. Measurements of $W_3(E)$ for CH_2Cl and $CHCl_2$ radicals in acetonitrile and water–dioxan mixtures showed that the displacement of the Tafel curve does not exceed 0.15 V, that is the difference in the relative values of pK in these solvents and in water is less than 5 units. It should be emphasised that the method[82] is universal, and does not lose its accuracy with increase in pK, and the range in which measurements can be made corresponds to the working range of potentials of the mercury electrode, and is greater than 30 pK units.

The range of change in W_3 in which the $W_3(E)$ relationships were measured for the CH_2Cl and $CHCl_2$ radicals[16] is greater than 10^6 (Fig. 14). The deviations from the Tafel law predicted by the theory of electron transfer in a polar medium[47,48] were not detected in this range. According to Marcus' model, the transfer coefficient for outer-sphere reactions in the range of normal discharge is a linear function of the overvoltage:

$$\alpha = \frac{1}{2} - \frac{e}{2E_s}(E^0 - E), \quad |e(E^0 - E)| < E_s. \tag{63}$$

Eqn. (63) shows that at $E_s \leqslant 200$ kJ mol^{-1}, corresponding to ELH reactions (see section IV), α should decrease from 0.5 to 0.30–0.25 in the measured range of E, but this does not agree with experiment. It was previously concluded from an analysis of the polarisation relationships in simple electrode reactions[92,93] that Eqn. (63) does not agree with experiment. The data of Benderskii and co-workers[16] confirm this conclusion; for the fulfilment of the Tafel law to agree with Eqn. (63), it is necessary to assume that $E_s \gtrsim 300$ kJ mol^{-1}, which is comparable with the solvation energy of the carbanions. This is contrary to the concept of a linearly polarised medium[94] on which the theory is based.[47,48] Benderskii and co-workers[16] suggested that the electron transfer is associated not only with reorganisation of the medium but also with reorganisation of the reaction complex itself. In the initial state, the adsorbed radical is in the compact part of the electrical double layer, where the water molecules are oriented by a strong electric field and cannot solvate the carbanion formed by electron transfer. Thus the solvation of the reaction product involves a displacement of the reagent along the adsorption coordinate in the direction of the Helmholtz plane. The existence of this reaction coordinate, associated with the desorption of the radical, which is necessary for solvation in the transition state, leads to the appearance of an additional energy of reorganisation. The combination of these two movements (of the radical and the medium) is similar to that examined[45] for ELH reactions, and leads to the relationship

$$\ln\frac{W_3}{W_3^0} = -\frac{(E_s + E_1 - e(E^0 - E))^2}{4E_s kT + rF^2\delta^2}, \tag{64}$$

where E_1 is the energy of reorganisation of the adsorbed radical, F the curvature of the carbanion term, $r^{-1} = 2\tanh(\hbar\omega/2kT) - 1$, and δ and ω are respectively the amplitude and frequency of the vibrations in the initial state. Eqn. (68) agrees with experiment for $E_1 \simeq E_s$. The value $E_s \simeq 150$ kJ mol^{-1} corresponds to the energy of reorganisation of the medium in the one-electron reduction of NO to NO^- (see section X), and explains why pK changes little with change in the solvent.

X. Intermediate species of the electrochemical nitrogen cycle

The electrochemical reduction of NO_3^- ions to NH_3 (the electrochemical nitrogen cycle) is an eight-electron process including the electronic stages of the formation of NO_2^- from NO_3^- ($n = 2$), NO from NO_2^- ($n = 1$), NH_2OH from NO ($n = 3$), and NH_3 from NH_2OH ($n = 2$). Each of these stages is associated with the transformation of short-lived IS: NO_3^{2-}, NO_2^{2-}, NO^-, H_2NO, and NH_2. Although the existence of these IS in aqueous solutions was

established by pulse radiolysis and EPR methods, their role in the nitrogen cycle was revealed only recently, by the LPE method.[95–98] The results are summarised in Fig. 15, and the rate constants of the homogeneous and electrode reactions of the IS are given in Tables 6 and 7.

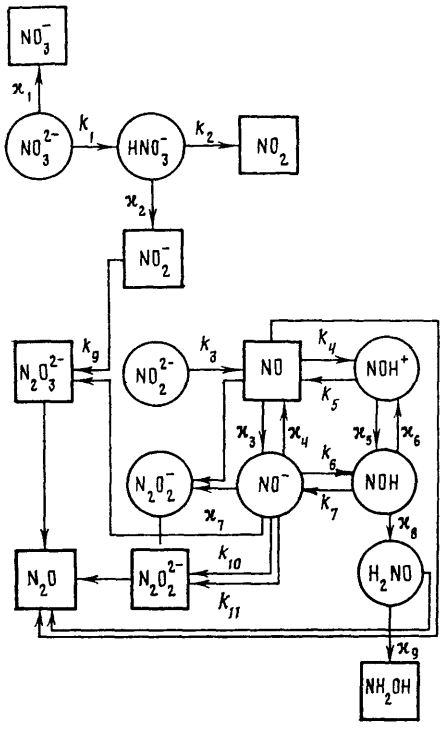


Figure 15. Homogeneous and electrode reactions of the IS of the electrochemical nitrogen cycle.

Table 6. Rate constants of the homogeneous reactions of the IS of the electrochemical nitrogen cycle.[96–98]

Reaction	K, mol^{-1} s^{-1}	Reaction	K, mol^{-1} s^{-1}
$NO_3^{2-}+H_2O \rightarrow HNO_3^-+OH^-$	$1\cdot10^3$	$NO^-+NH_4^+ \rightarrow NOH+NH_3$	$\sim10^6$
$NO_3^{2-}+NH_4^+ \rightarrow HNO_3^-+NH_3$	$2\cdot10^8$	$NO^-+H^+ \rightarrow NOH$	$\sim10^{10}$**
$NO_3^{2-}+H^+ \rightarrow HNO_3^-$	$2\cdot10^{10}$	$NO^-+NO \rightarrow N_2O_2^-$	$2\cdot10^9$
$HNO_3^- \rightarrow NO_2+OH^-$	$2.3\cdot10^5$*	$NO^-+NO_2^- \rightarrow N_2O_3^{2-}$	$\sim10^8$
$NO_2^{2-}+H_2O \rightarrow NO+2OH^-$	$9\cdot10^4$	$NO^-+NO^- \rightarrow N_2O_2^{2-}$	—
$NO+NH_4^+ \rightarrow NOH^++NH_3$	$\geqslant10^4$	$NOH \rightarrow NO^-+H^+$	$\sim10^6$*
$NOH^+ \rightarrow NO+H^+$	$>10^6$*	$H_2NO+NO \rightarrow H_2N_2O_2$	$\sim10^8$

* Unimolecular constant with dimensions s^{-1}. ** Estimate based on the value pK = 4.7 [99] and the rate constant of the dissociation of NOH.

Table 7. Rate constants of the electrode reactions of the IS of the electrochemical nitrogen cycle.[96–98]

Reaction	$-E$, V (NHE)	κ, cm s^{-1}	Transfer coefficient
$NO_3^{2-} \rightarrow NO_3^-+e^-$	0.76	1.5	0.25
$HNO_3^-+e^- \rightarrow NO_2^-+OH^-$	>0.8	$\geqslant$10	—
$NO+e^- \rightleftharpoons NO^-$	0.81	2	0.50
$HNO+e^-+NH_4^+ \rightarrow H_2NO+NH_3$	>1.0	>1	—
$H_2NO+e^++NH_4^+ \rightarrow NH_2OH+NH_3$	>1.0	>1	—

The product of the capture of e^-_{aq} by the nitrate ion is oxidised on mercury with a rate constant which increases from 0.1 cm s^{-1} to 10 cm s^{-1} with change in E from −1.2 V to −0.9 V (β = 0.25).[9] The oxidation competes with the homogeneous decompostion of the IS, for which the characteristic time is 1.3×10^{-5} s and 3×10^{-6} s for NO_3^{2-} and HNO_3^- respectively.[100] The decomposition product in the one-electron process is reduced. The charge of the IS oxidised was established[95] from the kinetic ψ_1-effect. At $\psi_1 < 0$, the electric field of the diffuse double layer retards the movement of the negatively charged IS towards the electrode. Since they have a finite lifetime in solution, this retardation increases the proportion of IS decomposing, compared with the proportion oxidised at the electrode, leading to an increase in the current and potential of the anodic half-wave of the IS. Analysis of the equations for the diffusion in the field of the ψ_1 potential of e^-_{aq} and the IS being oxidised leads to the relationship

$$j_1 = 2\frac{j-j_{\min}}{2-j_{\min}} = \left(1+\varkappa\sqrt{\frac{\tau}{D}}e^{-\Phi}+\frac{\varkappa x_0}{D\Phi}\right)^{-1}, \qquad (65)$$

where $j_{\min}$ is the minimum value of the current, corresponding to $\kappa \rightarrow \infty$, κ the rate of oxidation of the IS, τ the decomposition time of the IS, x_0 the characteristic dimension of the diffuse double layer, and $\Phi = \frac{eZ}{kT}\psi_1$, where Z is the charge of the IS. The second term in the denominator of Eqn. (65) characterises the ratio of the rates of the electrode reaction to the diffusion of the IS to the electrode under the condition of Boltzmann equilibrium, and leads to the Frumkin relationship[27]

$$\Delta E_{1/2} = (1+Z/\beta)\,\Delta\psi_1 \qquad (66)$$

which gives the dependence of the displacement of the half-wave potential of the species stable in solution on the ψ_1-potential. The third term, equal to the ratio of κ on the rate of the drift of the IS from the electrode into the solution, takes account of the deviation from equilibrium in strong fields, when the ψ_1-effect is due to the above-mentioned retardation of the IS. Eqn. (66) is applicable when $|\Phi| < \Phi^*$, where Φ^* is the solution of the equation $\Phi^*\exp(-\Phi^*) = x_0/\sqrt{D\tau}$, so that the applicability of the Frumkin equation depends on the lifetime of the IS in solution. The measured[95] displacement of the anodic wave in solutions with different ionic strengths, in which the ψ_1-potential changed from 0 to 0.09 V, corresponds to $Z = -2$, that is the primary IS is the NO_3^{2-} ion. It follows from the kinetic LPE curves that the characteristic time of the reduction of the product of the transformation of NO_3^{2-} does not exceed 2×10^{-7} s. The absence of an arrest corresponding

to the lifetime of HNO_3^- means that the decomposition of this ion (to give NO_2) does not precede the reduction, that is the species being reduced is HNO_3^-, and not NO_2. This conclusion[96] is confirmed by the fact that, judging from the rapid increase in the LPE signal, the rate of reduction is greater than 10 cm s^{-1} ($\kappa > \sqrt{D/\tau}$), whereas the reduction of NO_2 is a much slower process. The addition of different PD to the solution increases the rate of protonation of NO_3^{2-} (the rate constants are given in Table 6), and suppresses the oxidation wave. The published data[95,96] indicate that the electrochemical reduction of NO_3^- to NO_2^-, which is associated with a high overvoltage and is observed at $-E > 1.6$ V, involves the intermediate formation of the high-energy NO_3^{2-} ion, and, as a result of its rapid oxidation, is a quasi-equilibrium process. The decrease in the overvoltage in the presence of PD, which is also characteristic of various other anions,[101] is due to the increase in the rate of protonation, as a result of which NO_3^{2-} is converted into the HNO_3^- ion being reduced.

The wave for the one-electron reduction of the product of the capture of e_{aq}^- by the NO_2^- ion in neutral solution coincides with the polarographic reduction wave for NO. The characteristic reduction time found by the LPE method is greatest close to the half-wave potential and remains the same ($\sim 4 \times 10^{-7}$ s), independent of the NO_2^- concentration , at more negative potentials.[97] These data show that the species being reduced is NO, and the time for its formation in the decomposition of NO_2^{2-} is 2×10^{-7} s. The reduction of NO is reversible, since it is only if this is the case that the characteristic time, determined by the sum of the rates of the forward and back reactions, can be greatest when these rates are equal. The dependence of $E_{1/2}$ and the form of the wave on the frequency of the periodic photo-emission current Ω corresponds to the reversible reduction (see section IV) only at $\Omega > 10^2$ s^{-1}. At lower frequencies there is observed a component of the current due to subsequent irreversible transformations of NO^- with a characteristic time of $\sim 10^{-2}$ s, which depends on the bulk concentration of NO, proportional to the photo-emission current. These data correspond to the conversion of NO^- into $N_2O_2^-$ by reaction (8), whose rate constant has been measured.[101] In the one-electron reduction of $N_2O_2^-$, as in the bimolecular recombination of NO^-, the hyponitrite ion $N_2O_2^{2-}$ is formed, and its decomposition leads to the appearance of the final reduction product N_2O.

In the presence of PD, the extent of the reduction of NO increases from 1 to 3. The formation of NH_2OH in quantities corresponding to the photo-emission current and $n = 3$ was confirmed by chemical analysis.[98] In addition to the main wave, whose form and position are independent of n, a preliminary wave appears (see Fig. 4), whose height increases with increase in the PD concentration (N_p), reaching 3. Like the main wave, the preliminary wave is reversible. The fact that the values of n are the same for the preliminary wave and the main wave indicates that the reduction of NO to NH_2OH takes place by two parallel channels. The fact that the main wave is independent of N_p indicates that the process taking place by one of the channels, as in the one-electron reduction, includes the formation of NO^- and its protonation (the formation of NOH) and subsequent two-electron reduction. Since the preliminary wave lies in the range of E in which NO is reduced, the existence of the second channel is due to the formation of a new electrochemically active species in the reaction of NO with the PD. According to published suggestions,[102] this species is NOH^+. The height of the preliminary wave increases with decrease in Ω (see Fig. 4), so that the rate of protonation is of the order of Ω and the protonation is the limiting stage of the reduction. The $j(E, \Omega)$ relationship in the preliminary wave is described by the expression

$$j = \left| 1 + \frac{3}{1 + \sqrt{k_5 \Omega / 2 k_4^2}\,(1 + e^{-\eta}\sqrt{k_5/k_{10}})\sqrt{2i}} \right|. \quad (67)$$

Here, $\eta = \ln(\kappa_6/\kappa_5) = e/kT(E^0 - E)$, where E^0 is the standard NOH/NOH^+ potential, and the significance of the constants in Eqn. (67) can be seen from Fig. 15. Comparison of Eqn. (67) with the experimental data makes it possible to determine the ratio k_4^2/k_5, which was found to be equal to 10^2 s^{-1}. The $j(E)$ relationship, which corresponds to an effective transfer coefficient of 1, indicates that the reduction of NOH^+ is reversible. It follows from the kinetic LPE curves that the characteristic time of the two-electron reduction of NOH is $\sim 2 \times 10^{-6}$ s. The existence of an equilibrium between NO and NOH^+ means that $k_5 \gg k_{10}$ and the decomposition time of NOH^+ does not exceed 10^{-6}s, while $k_4 > 10^4$ mol^{-1} s^{-1}. The decrease in the height of the preliminary wave with increase in the NO_2^- concentration (N_a) indicates that NO^- and NOH react with NO_2^- according to Eqn. (9). The hyponitrate ion $N_2O_3^{2-}$ formed subsequently decomposes to give N_2O,[103] decreasing the extent of the reduction. The dependence of the limiting low-frequency current of the main wave on N_p and N_a, with allowance for the competition of the protonation of NO^- and reaction (9), has the form

$$j_n = 2(1 + (1 + k_7 k_9 N_a / k_8^2 N_p^2)^{-1}), \quad (68)$$

that is j_m depends on N_p^2/N_a, and $k_7 k_9 / k_8^2 \simeq 80$ mol. The nitroxyl radical H_2NO undergoes one-electron reduction at $-E > 0.2$ V (characteristic time less than 10^{-6} s).

Thus at high PD concentrations, NO is reduced quantitatively to hydroxylamine if the concentrations of NO_2^- and NO are so low that reactions (8), (9), and (11) which compete with the protonation do not interfere with the formation of NOH and the reduction of H_2NO. The scheme of transformations of the IS given in Fig. 15 provides a basis for the quantitative description of the concentration dependence, obtained from electrochemical measurements,[104] of the relative yield of the main products of the reduction of N_2O and NH_2OH. It follows from the scheme that only the protonated forms of the IS can be reduced, and that protonation precedes the electrode reaction. The protonation is apparently accompanied by the isomerisation of the IS. Since an O–H bond is formed in NOH^+, the reduction product is NOH. This species should be converted into the more stable form HNO,[105] and its subsequent reduction should also be associated with the formation of an O–H bond, and not N–H. The resulting IS HNOH (zerovalent nitrogen) undergoes isomerisation to H_2NO. It is this more stable radical that is observed in the gas phase[106] and in solution,[107] although in the oxidation of NH_2OH by the OH radical, HNOH is formed initially.[108] The suggestion that the IS undergoes isomerisation is consistent with the observed high rates of the electrode reactions (Table 7), since they are associated with the formation of O–H bonds, as in the rapid reduction of the radicals HCO_2 and HCO (see section VII).

The magnitude of the energy of rupture of the O–H bond in NH_2OH [106] shows that the standard H_2NO/NOH potential is greater than the NO^-/NO potential and that the quantitative transformation of NO into NH_2OH is determined by the latter; the reduction of HNO and H_2NO at $E < E^0$ for the NO^-/NO couple is isothermal. The quantitative transformation of NO into NH_2OH requires the expenditure of free energy (more than 234 kJ mol^{-1}). The standard NOH/NO potential, corresponding to $pK(NOH) = 4.7$,[101] is -0.54 V, so that the energy required for the reduction of NO to

NH_2OH in a standard solution with pH = 0 is greater than 155 kJ mol^{-1}, despite the fact that the process as a whole is exothermic (the standard NH_2OH/NO potential is +0.38 V).

The values of the ψ_1-potential appearing in Eqns. (65) and (66) coincide with the total decrease in the potential in the diffuse layer ψ_{10} only for dilute solutions ($\leqslant 10^{-2}$ M), where $x_0 \geqslant 2$ nm.[95] In more concentrated solutions, $|\psi_1| < |\psi_{10}|$. The difference between ψ_1 and ψ_{10} indicates that the NO_3^{2-} anion is discharged at a distance of 0.5–0.7 nm from the plane of maximum approach. The distance of electron transfer, which is several times greater than the geometric dimensions of the ion, is typical of tunnel reactions.[109] The probability of tunnel electron transfer from the reaction complex to the metal, W_0, is related to the rate constant of the oxidation by the simple expression $\kappa = W_0/a$, where a characterises the decrease in the electron density with increase in the distance. The values found[95] for κ correspond, in particular, to electron transfer through a parabolic barrier with a height of ~2 eV. As in ELH reactions (see section VI), the $\kappa(E)$ relationship is determined by the change in the height of the barrier with change in the potential.

The energy of reorganisation of the medium in the reduction of NO to NO^-, not associated with intramolecular rearrangement, can be estimated from the value of κ at $E = E^0$ using Marcus' equation[47] with a reasonable value of the pre-exponential term ($\leqslant 10^{14}$ s^{-1}). According to Benderskii and co-workers,[97] $E_s \simeq 135$ kJ mol^{-1}, which agrees with estimates of E_s in ELH reactions and in the reduction of organic radicals (section IX).

XI. Reduction of ions with anomalous valence

The homogeneous reactions of cations with anomalous valence have been studied in detail under pulse radiolysis conditions. Since the rate constants for the reduction of NO_3^-, NO_2^-, and hydroxyalkyl radicals by Zn^+, Ni^+, and Cd^+ ions are close to the diffusion values,[110] these reactions are exothermic, and the redox potentials for the formation of these ions from the divalent ions should be smaller than −1.5 V. According to published estimates,[111,112] $-E^0$ for the Ni^+/Ni^{2+} couple is greater than 1.8 V, and that for the Pb^+/Pb^{2+}- couple lies in the range 1.1–1.5 V. Comparison of E^0 with the half-wave potentials $E_{1/2}$ for the reduction of the corresponding divalent ions to the metal shows that the intermediate formation of the monovalent cations in this two-electron process is unlikely. According to LPE data the oxidation of the Cd^+, Zn^+, and Ni^+ ions on mercury in the range $E > E_{1/2}$ takes place in less than 10^{-7} s.

The many-electron reduction of anions has been studied by LPE for NO_3^-, NO_2^- (see section X) and BrO_3^-.[113–115] The product of the capture e_{aq}^- by the bromate ion is the BrO_2 radical, whose time-resolved polarograms (see Fig. 6) correspond to its five-electron reduction to Br^- with $E_{1/2} = -1.0$ V. An unexpected result is the value $j = 3$ in the range $E > E_{1/2}$, which formally corresponds to the one-electron reduction of the bromite ion BrO_2^-, although its half-wave potential is −0.88 V,[116] whereas $j = 3$ as far as $E = -0.3$ V, where the BrO_2^- ion is known to be electrochemically stable. The disproportionation of BrO_2^- to give BrO_3^- and BrO^- is also too slow to explain its reduction in 10^{-4} s. The observed increase in j is due to the ion–radical reaction

$$BrO_2 + BrO_2^- \rightarrow BrO + BrO_3^-, \qquad (69)$$

analogous to the transfer of O^- between the reagents, whose rate constants for exothermic reactions are close to the diffusion values.[117] Reaction (69) gives the BrO radical, which is reduced to Br^-, since the product of its one-electron reduction, that is the BrO^- anion, is electrochemically active at $E \leqslant 0$.[116] In reaction (69) with the subsequent three-electron reduction of BrO, only half of the BrO_2 radicals are converted into Br^-, that is $j = 3$. The scheme for the reduction of BrO_3^- at $E > E_{1/2}$ has the form:

$$BrO_3^- \xrightarrow{e^-} BrO_2 \xrightarrow{e^-} BrO_2^- \quad BrO \xrightarrow{e^-} BrO^- \xrightarrow{2e^-} Br^-. \qquad (70)$$

The kinetic LPE curves divide into sections, well separated in time, corresponding to the successive reduction of BrO_2 to BrO_2^- ($n = 1$, the characteristic time decreases from 3×10^{-6} s to 5×10^{-7} s in the range of E values from −0.70 V to −0.95 V) and of BrO^- to Br^- ($n = 2$, τ decreases from 4×10^{-3} s to 6×10^{-5} s in the range of E values from −0.4 V to −0.9 V). For $E < E_{1/2}$, the rate of the reduction of BrO_2^- is greater than the rate of reaction (69), so that $j = 6$. The kinetic LPE curves are described by the relationship

$$Q/Q_m = 6 - 4w(\varkappa_2 \sqrt{t/D}), \qquad (71)$$

where $\varkappa_2$ is the rate constant of the reduction of BrO_2^- to BrO, which is the limiting stage of the overall process.

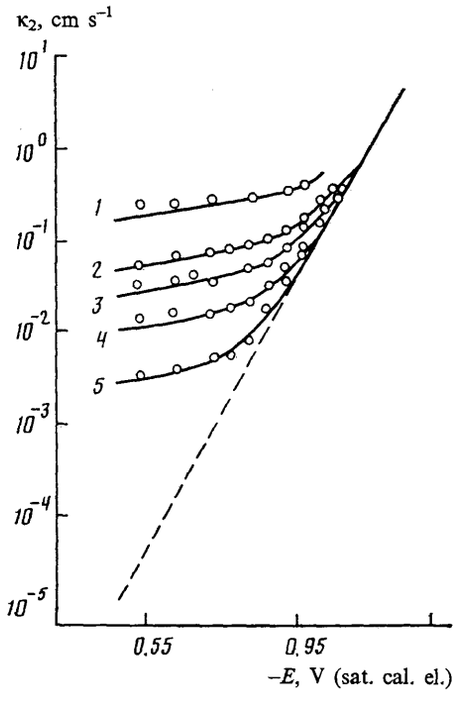


Figure 16. Dependence of the rate constant of the reduction of the BrO_2 radical on the electrode potential at NH_4^+ concentrations, M: *1*, 3.8×10^{-2}; *2*, 1.1×10^{-2}; *3*, 6×10^{-3}; *4*, 3×10^{-3}; and *5*, 1.5×10^{-3}; the broken straight lines corresponds to $N_p = 0$.[115]

Adding NH_4^+ ions to the solution leads to qualitative changes in the polarograms and the kinetic LPE curves. Increase in N_p is accompanied by an increase in $E_{1/2}$ and j for $E > E_{1/2}$ (for

$N_p > 7 \times 10^{-2}$ M, $j = 6$ throughout the working range of E), and the characteristic reduction time decreases rapidly. These changes are due to the increase in κ_2 as a result of the participation of PD in the electrode reaction

$$BrO_2^- + e^- + NH_4^+ \rightarrow BrO + OH^- + NH_3. \quad (72)$$

The $\kappa_2(E)$ relationships for different N_p are given in Fig. 16, and confirm the published conclusion[100,118] that PD take direct part in the reduction of the anions. The rate constant of reaction (72) depends little on E and is close to the diffusion value (~ 5 cm s^{-1}).

XII. Summary

The examination of the electrochemistry of IS opens up new possibilities in the study of both complex many-electron transformations at an interface and the elementary stage of electrode reactions. The significant role of intramolecular reorganisation on electron transfer means that Marcus' model, which takes account of only the reorganisation of the polar medium and for this reason claims to be universal, should be supplemented by an examination of the rearrangement of the reaction complex itself and its solvate layer. In the present state of quantum chemistry, these calculations are becoming possible. Allowance for these last processes may lead to fundamental changes in existing ideas, since reorganisation of this kind (like reorganisation of the medium) not only creates a dynamic barrier to transfer but also leads to the production of a nuclear configuration favourable for reaction. This last feature, in particular, is the factor responsible for rapid low-temperature solid-phase transformations,[119] and possibly plays an equally important role in electrode reactions. The formation of high-energy IS (derivatives of carbene, carbanions, biradicals, etc.), detected by PECR and LPE methods in many electrode reactions, also requires further experimental and theoretical study. The development of these new methods should lead in turn to the development of more selective polarographic analysis, compared with the polarography of stable species.

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The parameters of the ^{13}C NMR spectra of substituted acetylenes: relation with electronic structure and reactivity

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ABSTRACT. Questions concerning the electronic structure of the ethynyl fragment and the effectiveness of its interaction with various heteroatomic and unsaturated substituents are examined on the basis of the analysis of an extensive set of parameters of the ^{13}C NMR spectra of mono- and di-substituted acetylenes. The additive influence of the two substituents in disubstituted acetylenes on the shielding of the *sp*-carbon atoms, due to the counterpolarisation of the orthogonal π-systems of the triple bond, is demonstrated. The question of the possible use of the ^{13}C NMR spectral parameters for the estimation of the reactivity of the triple bond is discussed.

The bibliography includes 140 references.

Contents

I. Introduction 23
II. Chemical shifts of the ethynyl ^{13}C atoms 23
III. The constants for the spin–spin coupling in the acetylenic fragment 31
IV. Relation between the reactivity of substituted acetylenes and the chemical shifts of the ethynyl carbon atoms 32

I. Introduction

The unique reactivity of acetylenic compounds is responsible for their extensive use in thermographic synthesis—both in laboratory practice and in industry. However, the development of theoretical aspects of the behaviour of acetylenic compounds in reactions lags significantly behind practical advances. The extensive employment (in careful analysis and survey of results of studies on acetylenes themselves and on the reactions with their participation) of instrumental physical methods combined with theoretical quantum-chemical methods should help to overcome this discrepancy.

The ^{13}C NMR spectroscopy with its modern apparatus (Fourier transformation, the application of multipulse sequences, ultra-high magnetic fields) is one of the most universal methods for the study of the electronic and geometrical structures of organic and organo-element molecules and it has the highest information content. Its possibilities as regards acetylenic compounds are simple unique. Indeed, of the six parameters of NMR spectra with the aid of which it is possible to characterise the terminal ethynyl fragment of monosubstituted acetylenes [the chemical shift δ and the spin–spin coupling constants (SSCC or *J*): one ^{1}H chemical shift, two ^{13}C chemical shifts, two $^{13}C-^{1}H$ SSCC, and one $^{13}C-^{13}C$ SSCC], five can be obtained from the ^{13}C NMR spectrum and in the case of disubstituted acetylenes the entire spectroscopic information about the triple bond and about the carbon atoms involved in it is contained in the ^{13}C NMR spectrum. Since the chemical shifts of the acetylenic proton in monosubstituted acetylenes are exceptionally sensitive not only to intramolecular effects but also to solvation effects, they will not be considered in this review. The constants for the spin–spin coupling of this proton with the ^{13}C nuclei are more characteristic and permit an unambiguous assignment of the ethynyl carbon atoms in the ^{13}C NMR spectrum and they are therefore discussed in this review together with the $^{13}C-^{13}C$ SSCC. Here and henceforth the relaxation times of the nuclei and isotope substitution effects will not be considered.

II. Chemical shifts of the ethynyl ^{13}C atoms

1. General features and formulation of the problems

Whereas the number of known values of δC for the carbon atoms in certain unsaturated hydrocarbon fragments, for example in the benzene ring or in the double bond, reaches several thousands, the number of δC for acetylenic compounds is smaller by an order of magnitude. Most of the data refer to alkynes, alkynols, and compounds having the general formula $R_3EC{\equiv}CH$, where E = Si, Ge, or Sn.

The signals of the ethynyl carbon atoms in the ^{13}C NMR spectra are manifested in the range 65–95 p.p.m. [relative to the signal of the carbon atom in tetramethylsilane (TMS)], which is intermediate between the regions characteristic of the ^{13}C nuclei of the sp^3- and sp^2-carbon atoms. The alkyl groups attached to the triple bond shield the C_β atoms and deshield the C_α atoms, inducing changes in the shift of approximately 4–6 and 10–20 p.p.m. relative to δC for acetylene (72.0 p.p.m.).[1] Calculation of the distribution of charges in 1-alkynes by the CNDO/2 method has shown[2] that mainly the polarisation of the triple bond takes place under the influence of the alkyl substituent. In disubstituted acetylenes, the influence of two alkyl groups on δC is additive and quantitative estimates of the contributions of the groups having normal[3,4] and branched[5] structures are available. A topological scheme has been developed for highly accurate calculations (±0.6 p.p.m.) of δC_{sp} for alkynes and alkynols from data for 86 compounds.[5,6] A characteristic feature of the influence of the Alk_3E (E = Si, Ge, Sn) groups on the chemical shifts of the C_{sp} atoms is the deshielding of both carbon atoms (an average shift of 20 p.p.m.), which is explained by the appreciable π-acceptor effect of the Alk_3E groups ($p_\pi-d_\pi$ or $p_\pi-\sigma^*$ conjugation).[7–12] The acceptor properties of the silicon atom in relation to the triple bond have been confirmed by calculations of

the charge distribution.[12,13] The influences of the X and Me_3E groups on δC_{sp} are independent within series of compounds with identical E and can be described to a first approximation by the Hammett–Taft equation.[7] This conflicts with the results of studies of substituted hexynes $Bu^nC\equiv CX$, for which the absence of a relation between δC and the induction and resonance characteristics of the groups X has been noted.[14] In a number of cases a relation has been observed between the kinetic parameters of the reactions involving addition to acetylenic compounds and the σ-constants of the substituents (see, for example, Refs. 15–19). It is noteworthy that, whereas the AlkO groups of ethynyl ethers shield anomalously strongly the β-carbon atom, the AlkE groups, where E = S, Se, or Te, actually deshield it, which is explained by the reduced capacity of these chalcogens for p_π-interaction and the dominant influence of the d_π-acceptor properties.[7,20–22] The above features require refinement, because all chalcogens exhibit π-donor properties in relation to vinyl and phenyl fragments.[23]

Limited information is available about the chemical shifts of the ^{13}C atoms in acetylenic compounds containing boron,[24,25] phosphorus,[7,20,21,26] and the halogens.[7,14] The R_2P and R_2PO groups deshield the C_β atom to virtually equal extents (a 20 to 25 p.p.m. shift), whereas their effects on C_α are different: shifts of 10–15 and 2–8 p.p.m. respectively are observed. This has been explained by the π-acceptor effect of the phosphorus-containing substituents on the triple bond.[20,21,26] The R_2P group acts similarly on the triple bond. In the series of halogen-substituted acetylenes, the changes in δC are very great: on passing from Cl- to I-substituted compounds, the shielding of C_α increases by 60 p.p.m., while that of C_β diminishes by 30 p.p.m.; the values of δC_β for iodoacetylene derivatives exceed 100 p.p.m., while the values of δC_α are close to 0 p.p.m.[7,14] The explanation of changes in δC of this kind by the effect of anisotropy[27] or intermolecular dispersion interactions[28] is hardly acceptable.

The available information about δC for acetylenic compounds containing other substituents, including unsaturated ones, is even more scanty and is less susceptible to unambiguous interpretation. Analysis of the ^{13}C NMR spectra of several substituents in the ring of phenylacetylenes permitted the hypothesis that the π-electron systems of the triple bond and the aromatic ring do not interact at all,[29] although in another study[30] the field, resonance, and π-induction effects of the substituents were accepted as determining the charge distribution on the triple bond carbon atoms. The hypothesis that the lower sensitivity of the shielding of C_{sp} compared with C_{sp^2} to changes in charge density may be the counter-polarisation of the triple bond has been put forward.[30] This was first suggested when the changes in δC_{sp} and δC_{sp^2} for arylpropynes and arylpropenes were compared.[31] The possibility of the counterpolarisation of the π-electron systems of the triple bond follows from the results of the non-empirical calculation for the hypothetical aminoacetylene molecule.[32] All these features agree with the results of the analysis of the integral intensities of the triple bond bands in the IR spectra as a measure of their resonance interaction in monosubstituted[33,34] and disubstituted[35] acetylenes, indicating a lower sensitivity of the triple bond, compared with the double bond, to the resonance effect, although the resonance interactions in acetylenic compounds involve both π-systems of the triple bond.

The question of the transmission of the π-electronic perturbations through the triple bond remains obscure. Comparison of the reactivities of the group Y in the $p\text{-}XC_6H_4-M-C_6H_4Y\text{-}p$ bridged systems has shown[36] that similar coefficients for the transmission of the π-electronic perturbations are characteristic of molecules with M = $-CH=CH-$ and $-C\equiv C-$ bridges (0.89 and 0.82 respectively). On the other hand, there is evidence that the effects of the Alk_3E (E = Si, Ge, and Sn) groups are transmitted to an extremely slight extent across the triple bond to the neighbouring $C=C$[10] and $C=O$[11] double bonds.

Among general features, we may note the hypothesis of Rosenberg and co-workers,[20,21] according to which the sum of the values of δC_{sp} characterises the overall charge on the triple bond and their difference characterises its polarisation. Doubts were subsequently cast on the legitimacy of this conclusion.[22]

Thus analysis of the literature data permits the formulation of the following key questions concerning δC_{sp} for acetylenic compounds:

(1) how independent of one another are the effects of two substituents on the shielding of ethynyl carbon atoms;

(2) what is the relation between the charge distribution and the chemical shifts of the carbon atoms in the triple bond;

(3) what are the mechanisms of the interaction of various heteroatomic and functional groups with the triple bond;

(4) to what extent is the model of the counterpolarisation of the triple bond justified;

(5) to what extent are the electronic effects of the substituents transmitted through the triple bond;

(6) is there a relation between the parameters of the ^{13}C NMR spectra and the reactivity of the triple bond.

In the analysis of experimental results, we used three main approaches: (a) comparison of NMR data with the results of quantum-chemical calculations for the molecules; (b) correlation analysis based on the principles of the linearity of free energies (LFE) and polylinearity (PPL) as a quantitative theory of organic chemistry; (c) comparison of the values of δC for the corresponding derivatives of ethane, ethylene, and acetylene.

2. Analysis of the joint effect of substituents on the chemical shifts of ^{13}C atoms in disubstituted acetylenes

The independent effects of the substituents on δC for the triple bond is a characteristic feature of certain series of disubstituted acetylenes—alkynes,[5,6,37] phosphorus derivatives,[26] and silicon, germanium, and tin derivatives.[7] This made it possible to determine the additive contributions of the individual substituents in the calculation of δC_{sp}.[38,39] A survey of all the available δC data (1184 values) showed[40,41] that the nature of the groups R^1 and R^2 in the compounds $R^1C\equiv CR^2$ influences δC and induces changes in it in the range of approximately 100 p.p.m. General relations taking into account the simultaneous changes in the structures of R^1 and R^2 within the framework of the polylinearity principle have been found.

According to the polylinearity principle, δC† can be formulated as follows:[40]

$$\delta C(R^1C\equiv CR^2) = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2, \quad (1)$$

where X_1 and X_2 are quantitative characteristics of the structures of R^1 and R^2 respectively, a_0, a_1, a_2, and a_{12} are coefficients, and $a_{12} \neq 0$ only when the effects of R^1 and R^2 are non-additive. It has been shown,[40] that the applicability of Eqn. (1) is determined by the applicability of the LFE principle to δC_{sp}. The absence of a cross term in Eqn. (1) requires that the following simple relation should

† Here and henceforth we have in mind δC_{sp} for the detector atom—the carbon atom at the substituent R^1.

hold between the values of δC for disubstituted acetylenes and the corresponding monosubstituted acetylenes:

$$\delta C(R^1C{\equiv}CR^2) = a_0 + a_1[\delta C(R^1C{\equiv}CH) + \delta C(HC{\equiv}CR^2)], \quad (2)$$

where a_0 = δC(HC−CH) and a_1 = 1.00.

Fig. 1 presents the theoretical relation (continuous line) corresponding to Eqn. (2) on which the experimental data for 369 acetylenic compounds have been plotted (of these, 366 refer to disubstituted acetylenes). A satisfactory agreement is observed between the theoretical straight line and the experimental data, which is indicated by the high statistical parameters of the equations:

$$\delta C(R^1C{\equiv}CR^2) = -75.60\,(1.13) + 1.02\,(0.007)\,[\delta C(R^1C{\equiv}CH) + \delta C(HC{\equiv}CR^2)],$$
$$r = 0.992,\ s = 1.98,\ n = 369. \quad (2a)$$

For points whose deviations from the theoretical straight line are ⩽ ⩽43.0 p.p.m., we have

$$\delta C(R^1C{\equiv}CR^2) = -74.60\,(0.91) + 1.01\,(0.006)\,[\delta C(R^1C{\equiv}CH) + \delta C(HC{\equiv}CR^2)],$$
$$r = 0.995,\ s = 1.43,\ n = 334, \quad (2b)$$

where r is the correlation coefficient, s the standard deviation, and n the number of points included in the correlation. The coefficients a_0 and a_1 in these equations have values close to theoretical ones. A further improvement of the quality of the description is pointless, since the accuracy with which the LFE principle is maintained for $\delta C(R_1C{\equiv}CR^2)$ does not exceed ±1.3 p.p.m.[40] For 24 of the most common substituents R^1 and R^2, a resultant matrix has been set up and their additive contributions Δ to the shielding of the C_α and C_β atoms attached to the triple bond have been calculated. The regression equation obtained

$$\delta C(R^1C{\equiv}CR^2) = 72.0 + \Delta\delta C_\alpha(R^1) + \Delta\delta C_\beta(R^2) \quad (3)$$

permits the calculation of δC_{sp} for 576 of the corresponding acetylenic compounds with an accuracy not less than to within 2.0 p.p.m.[42] The additive contributions are listed in Table 1. The application of the additive scheme permits a significant simplification of the assignments of the ^{13}C signals in disubstituted acetylenes and is extremely useful for the theoretical calculation of the δC for the ethynyl carbon atoms.

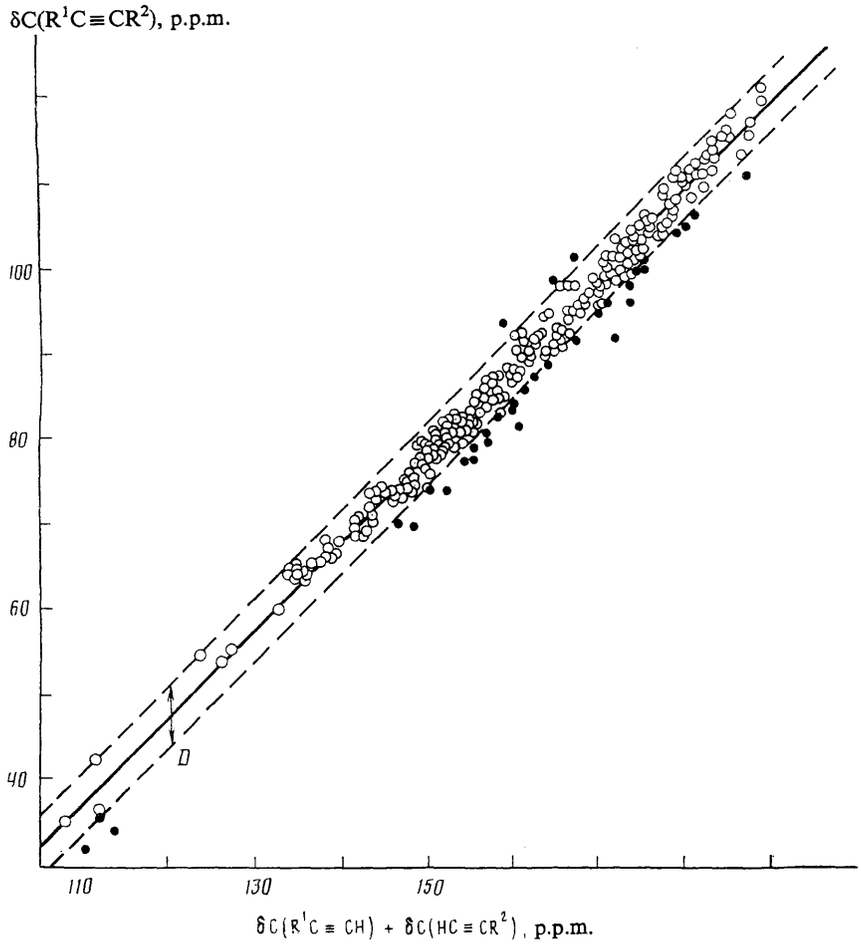


Figure 1. Dependence of the experimental shifts $\delta C(R^1C{\equiv}CR^2)$ on the theoretically calculated sums $\delta C(R^1C{\equiv}CH) + \delta C(HC{\equiv}Cr^2)$ (according to the results of Kalabin and co-workers[40,41]): *D* is a ±3 p.p.m. "corridor" around a theoretical straight line; ●—points whose deviations exceed 3.0 p.p.m.; ○—points corresponding to experimental data whose deviations from the theoretical straight line do not exceed 3.0 p.p.m.

The reliable establishment of the fact that the substituents have additive effects on the δC for acetylenic compounds is extremely useful for utilitarian purposes, but it is somewhat unexpected, since it presupposes the absence of interactions between the substituents R^1 and R^2. Together with disubstituted acetylenes, model *trans*-1,2-disubstituted ethylenes and 1,4-disubstituted benzenes were also examined. These are the simplest unsaturated compounds where there is no steric interaction between the substituents but there is an effective interaction via the mechanism involving direct polar conjugation.[29,42–47]

In order to discover how the interaction of the substituents is manifested in such substituted benzenes and acetylenes, the values of δC for these series of compounds were subjected to a statistical treatment within the framework of the corresponding mathematical model.[41,48] In *trans*-1,2-disubstituted ethylenes and 1,4-disubstituted benzenes, the influence of the substituents R^1 and R^2 is significantly non-additive. In the compounds $R^1C{\equiv}CR^2$, the substituents R^1 and R^2 influence the chemical shift δC_{sp} independently of one another, and their effects are described satisfactorily within the framework of the polylinearity principle. The additivity of the effects of the substituents on the δC for ethynyl carbon atoms in disubstituted acetylenes presupposes the absence of direct interaction between the substituents through the triple bond. The possibility of the constancy of the contribution of such interaction appears unlikely.

Table 1. The additive contributions of the substituents to the shielding of the $^{13}C_{sp}$ nuclei in disubstituted acetylenes.[42]

R^1	$\Delta\delta\ C_\alpha$	$\Delta\delta\ C_\beta$	R^1	$\Delta\delta\ C_\alpha$	$\Delta\delta\ C_\beta$
H	0.0	0.0	Me_3Si	17.6	23.1
Me	7.8	—4.4	Et_3Si	15.6	23.8
Et	13.4	—4.1	Me_3Ge	17.5	21.4
Bu	13.0	—3.3	Et_3Ge	14.9	23.2
Bu^t	20.6	—5.6	Me_3Sn	15.7	26.8
Ph	12.0	6.0	Et_3Sn	14.2	26.8
p-$MeOC_6H_4$	11.9	4.9	$P(O)(OEt)_2$	1.6	17.0
p-MeC_6H_4	11.9	5.5	C≡N	—15.9	3.2
p-ClC_6H_4	10.6	7.0	COMe	10.8	6.7
$CH_2{=}CH$	9.9	6.7	COPh	9.0	9.3
$Me_2C(OH)$	17.5	0.2	OEt	16.2	—52.3
CH≡C	—3.3	—7.2	SEt	0.5	11.2

Note. The error of the determination of the contributions does not exceed ±2.0 p.p.m.

The non-additivity of the effects of substituents on δC_{sp^2} for *trans*-1,2-disubstituted ethylene derivatives is very considerable. The maximum deviations of δC from values calculated on the assumption of additivity reach 30 p.p.m. Although the deviations from additivity are much smaller for disubstituted acetylenes, (the number of compounds for which experimental δC deviate by more than 3.0 p.p.m. from the theoretical values is 27 and 3% of the total number for *trans*-disubstituted ethylenes and disubstituted acetylenes respectively[41]), analysis of these deviations can throw light on the nature of this phenomenon. Table 2 presents compounds for which the values of δC_{sp} for R^1 differ by more than 3.0 p.p.m. from the values calculated theoretically by Eqn. (2). If one excludes from consideration compounds 5 and 6 (data obtained in H_2O[49]), it is found that out of 31 compounds, 28 compounds (>90%) have substituents $ER^1R^2R^3$, where E = Si, Ge, Sn, or P, which is undoubtedly not fortuitous. We shall consider in greater detail the cause of the observed phenomenon.

3. The counterpolarisation of the π-systems of triple bonds

The π-electron systems of the triple bond in acetylene are energetically degenerate, i.e. the π-charge is distributed along the axial position relative to the molecular axis. Depending on the symmetry, the substituents remove this degeneracy to a greater or lesser extent. The degeneracy is apparently removed to the least extent by alkyl substituents and halogen atoms, in the presence of which the molecular symmetry is close to C_{3v} and the barrier to rotation is low. The non-equivalence of the π-orbitals of the triple bond increases with increase in this barrier, reaching a maximum for substituents having a symmetry plane (the COR, Ph, $CH{=}CH_2$, etc. groups). Such substituents are capable of interacting only with one of the π-systems of the triple bond, polarising it or becoming conjugated with it (an appreciable π-charge transfer takes place). The polarisation of the second, orthogonal π-system can partly compensate for the redistribution of the π-charge in the first system, i.e. the counterpolarisation of the orthogonal π-systems of the triple bond takes place. The possibility of this phenomenon has been stated in a number of studies[29–31] (see above).

Table 2. The deviations (*D*, p.p.m.) of the experimental shifts δC for the compounds $R^1{-}C{\equiv}C{-}R^2$ from the calculated values.[41]

Compound	R^1	R^2	*D*	Compound	R^1	R^2	*D*
1	Et_3Ge	n-C_6H_{11}	—4.2	17	*p*-FC_6H_4	$P(O)(OEt)_2$	—4.9
2	Et_3Sn	n-C_6H_{11}	—5.2	18	Ph	$P(O)(OEt)_2$	—4.2
3	Et_3Sn	n-Bu	—3.7	19	*p*-MeC_6H_4	$P(O)(OEt)_2$	—4.4
4	Me_3Si	CH_2CH_2OH	—3.8	20	*p*-ClC_6H_4	$P(O)(OEt)_2$	—5.2
5	$HOCH_2$	$CH_2[\overset{\oplus}{N}Me(Et)_2]\overset{\ominus}{I}$	—8.1	21	*p*-$MeOC_6H_4$	$P(O)(OEt)_2$	—4.0
				22	Ph	C≡N	—3.2
6	$\overset{\ominus}{I}[(Et)_2\overset{\oplus}{M}eNCH_2]$	CH_2OH	—5.8	23	$HOCH_2$	C≡CPh	—3.8
7	Me_3Si	CH_2OH	—3.2	24	Me_3Sn	OEt	—6.7
8	Et_3Ge	$CH_2N(CH_2)_4O$	—7.1	25	Me_3Ge	C_6F_5	3.6
9	Et_3Ge	$CH_2N(CH_2)_5$	—3.7	26	Me_3Si	C≡N	4.9
10	Et_3Si	$CH_2N(CH_2)_4O$	—3.2	27	Me_3Sn	C≡N	6.5
11	PhC(O)	C(O)Ph	—4.6	28	N≡C	$SnMe_3$	—3.1
12	Me_3Si	OEt	—4.0	29	Et_3Ge	Bu^t	—3.1
13	Et_3Ge	COH	3.9	30	Me_3Sn	Bu^t	—4.7
14	Et_3Ge	COMe	4.3	31	Et_3Sn	Bu^t	—3.8
15	Me_3Ge	OEt	—4.6	32	Me_3Sn	Et	—3.3
16	Et_3Sn	OEt	—6.5	33	Me_3Si	$SnMe_3$	3.2

If each substituent in disubstituted acetylenes interacts with only one π-electron system of the triple bond, then the effectiveness of the interaction between the substituents themselves can be minimal and their effects on the triple bond can be entirely independent. The observed additivity of the effects of substituents confirms these ideas. The substituents in disubstituted ethylenes and benzenes interact with one π-system and their effects cannot be independent. The non-additivity of the effects of substituents on δC_{sp^2} in these systems can therefore be also understood.

The general features of the influence of substituents on the shielding of ethynyl carbon atoms can be formulated on the basis of the counterpolarisation idea in the following manner.

1. If the substituent interacts with one only π-system of the triple bond, then, as a result of the counterpolarisation, its effect on δC_{sp} is equal to or smaller than its effect on a double bond.

2. If the substituent interacts simultaneously with both π-systems of the triple bond, then counterpolarisaiton is difficult and its effect on δC_{sp} is equal to or greater than its effect on a double bond.

3. The greatest deviations from additivity are characteristic of disubstituted acetylenes in which one of the substituents is capable of interacting with both π-systems, while the other, regardless of symmetry, exerts a complementary or competitive π-electronic effect.

The latter is confirmed by the data in Table 2: the electron-accepting properties of Si, Ge, Sn, and P in relation to the π-system depend little on the angles of rotation of the corresponding substituent relative to the multiple bond.[50] For this reason, one should expect appreciable deviations for ethynyl ethers, in which the oxygen atom has a π-donor capacity in relation to both orthogonal π-systems.[33] Finally, the orthogonal orbitals of neighbouring triple bonds also interact with one another in the same way.

Table 3. The influence of various substituents (ΔδC) on the shielding of the α- and β-carbon atoms of the double and triple bonds in monosubstituted derivatives of ethylene and acetylene.

R	R–CH=CH₂		R–C≡CH		Presence of counter-polarisation (+, –)	σ_R^0	$(\sigma_R^0)_{tw}$
	Δδ C_α	Δδ C_β	Δδ C_α	Δδ C_β			
Me	3.2	–16.6	–2.9	–14.7	+	–0.10	–0.10
Bu^t	–0.3	–16.3	–10.7	–7.8	+	–0.13	–0.13
EtO	–3.1	–47.0	–42.8	–58.5	–	–0.44	–0.23
EtS	–10.9	–23.2	–20.0	–0.5	+	–0.25	–0.05
Et_3Si	16.1	8.0	18.5	23.1	–	0.03	0.03
N≡C	–10.4	13.6	–10.1	4.4	+	0.10	0.10
CH_3=CH	–16.1	–22.9	–20.0	–10.3	+	—	—
Ph	–7.6	–20.7	–10.1	–6.0	+	–0.10	–0.06
HOC	–15.8	14.6	–21.9	11.7	+	0.24	0.0
HOOC	–16.4	7.1	–19.2	2.2	+	0.29	0.0
Cl *	–29.8	–18.5	–45.3	–27.9	–	–0.22	–0.22
$(OEt)_2(O)P$ *	0.7	11.6	2.1	16.0	–	—	—
Me_2N *	–25.2	–44.0	–25.1	–28.8	+	–0.53	–0.13

Note. Effects relative to saturated compounds are indicated, i.e. $\Delta\delta C_{sp^2(sp)} = (\delta C_{sp^2(sp)} - \delta C^0_{sp^2(sp)}) - (\delta C_{sp^3} - \delta C^0_{sp^3})$. The values $\delta C^0_{sp}(HC\equiv CH) = 72.0$, $\delta C^0_{sp^2}(CH_2=CH_2) = 122.8$, and $\delta C^0_{sp^3}(CH_3CH_3) = 5.7$ were used.

* The estimate was made for 1,2-trans-disubstituted ethylenes and disubstituted acetylenes.

The first two postulates have been confirmed by the analysis of the relative effects of different substituents on the shielding of α- and β-carbon atoms of the multiple bond in vinyl and ethynyl compounds (Table 3). The Table also indicates the resonance constants of the substituents α_R^0 and $(\sigma_R^0)_{tw}$,[33] which correspond to the interaction of the substituents with the two orthogonal π-systems of the triple bond. The signs of these constants are always the same but the constants $(\sigma_R^0)_{tw}$ are equal to or smaller than σ_R^0. The numerical values of the constants indicate a non-equivalence, in certain cases, of the π-systems of triple bonds and the possibility of their counterpolarisation. Table 3 does not include data for compounds with R = $GeEt_3$ and $SnEt_3$, since they are identical with data for R = $SiEt_3$. All the results, with the exception of those which correspond to compounds with the EtS and N≡C groups, are fully consistent with the model of the counterpolarisation of the triple bond π-orbitals developed here.

The fact that the concept of the counterpolarisation of the triple bond is well founded has been confirmed by the calculation of the distribution of π-electron densities in a series of model acetylenic compounds, which have been performed by non-empirical methods using the OST-4GF basis set (Table 3). The countertransfer of the π-charge via the orthogonal π-systems of the acetylenic fragments has been noted for aminoacetylene, formylacetylene, and phosphinoacetylene molecules‡, i.e. in the presence of substituents (π-donor and π-acceptor) capable of direct interaction with only one π-system of the triple bond.

The fluorine atom interacts effectively with both triple bond π-systems. This gives rise to the maximum transfer in the given instance of the negative π-charge to the terminal carbon atom of the triple bond and also agrees with experiment.

The presence of two hybrid orbitals with different symmetries, which include the unshared electron pairs of the oxygen atom in hydroxyacetylene, is responsible for the effective interaction of one of the unshared electron pairs in the case of a planar molecular conformation, whereas the contribution of a second electron pair to the corresponding π-MO is much smaller and compensates for the possible countertransfer of the charge (Table 4).

Table 4. The distribution of charge density ($10^3 q_\pi$) in the acetylenic fragment of the compounds $H-C_\beta\equiv C_\alpha-X$.[41]

X	q_{C_α}			q_{C_β}		
	π_y	π_z	Σπ	π_y	π_z	Σπ
H	0	0	0	0	0	0
$CH=CH_2$	1	16	17	–6	–20	–26
CHO	–16	16	0	36	–15	21
COOH	–19	1	–18	36	4	40
NH_2 (planar molecule)	–48	58	10	44	–134	–90
NH_2 (non-planar molecule)	–31	38	7	21	–93	–72
PH_2	31	–51	–20	–25	26	1
OH	19	–30	–11	–79	1	–78
F	–28	–28	–56	–48	–48	–96

The results presented in Tables 3 and 4 make it possible to estimate the sensitivity of the chemical shifts of the *sp*-carbon atoms to π-electronic effects (it amounts to 600 p.p.m. per charge unit, which is approximately three times greater than the analogous characteristic of the sp^2-carbon atoms of substituted ethylenes).

Overall, the results of quantum-chemical calculations for monosubstituted acetylenes, the analysis of the chemical shift δC_{sp} for mono- and di-substituted acetylenes, and their comparison with the analogous results for disubstituted ethylenes indicates the occurrence of the counterpolarisation of the orthogonal π-systems of the triple bond.

‡ The calculation for the phosphinoacetylene molecule was performed in terms of the *sp*-basis set (without taking into account the *d* orbitals) and the phosphorus atom therefore behaves as a π-donor as a result of the presence of its unshared electron pair.

4. The ability of the triple bond to transmit the effects of substituents

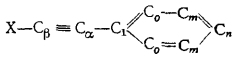
We shall consider the character and degree of the transition of the electronic effects of the groups X through the triple bond in relation to the compound X−C≡C−R, where R = Ph, $CH=CH_2$, or C≡CH. In vinylacetylenes $X-C_\alpha\equiv C_\beta-C^1H=C^2H_2$,[51–53] there is no explicit relation between the changes in δC_β and δC^2. One may note that the effect of X on the triple bond is specific, since the substituent X induces a displacement of δC_β by more than 40 p.p.m., whereas δC^2 is displaced by only 4 p.p.m. and δC^1 by only 2 p.p.m. The effect of X on the terminal vinyl group is mainly manifested by the polarisation of π-electrons by the dipole of the X−C bond (the changes in δC^1 and ΔC^2 take place in the opposite directions and agree with the direction of the dipole). This can be seen from a comparison of the δC for the two compounds $Et_2NCH_2C_\alpha\equiv C_\beta-C^1H=C^2H-SEt$ (A) and $[Et_2MeNCH_2-C_\alpha\equiv C_\beta-C^1H=C_2H-SEt]I$ (B):[54]

	C_α	C_β	C^1	C^2
δC(A), p.p.m.	92.4	81.6	104.9	139.6
δC(B), p.p.m.	87.2	84.1	101.9	144.8
Δδ C	−5.2	2.5	−3.0	5.2

The results presented as well as the available data for diacetylenic compounds[53,55–57] agree fully with the model involving a significant polarisation of the triple bond.

The ability of the triple bond to transmit electronic effects to the benzene ring can be characterised and the degree of interaction of the ethynyl and phenyl groups can be elucidated most correctly by analysing the data for β-substituted phenylacetylenes X−C≡CPh. This series of compounds is attractive because the values of δC for the compounds X−Ph are known for virtually any groups X and the $Ph-C_\alpha\equiv C_\beta-X$ fragment has a rigid conformation, while the presence of four indicator centres in the benzene ring facilitates the classification of the effects of the group X.

The values of δC for 39 β-substituted phenylacetylenes



have been published.[41] As for other series of compounds, not even a qualitative relation is observed in this instance between the δC_{sp} and any of the sets of the σ constants of the group X. We shall consider the characteristics of the variation of the degree of shielding of the aromatic carbon atom. The changes in the latter amount to 9.2, 10.0, 4.0, and 18.0 p.p.m. for C_1, C_o, C_m, and C_p respectively. The effect of the substituent X on the shielding of the C_{sp^2} atoms in the compounds X−C≡C−Ph is formally of the same type,[41] which follows from the equation

$$\delta C_m = 0.183(0.006)\delta C_p + 104.9(0.8),\quad r = 0.985,\ s = 0.14;$$
$$\delta C_o = 0.545(0.018)\delta C_p + 61.5(2.3),\quad r = 0.981,\ s = 0.41;$$
$$\delta C_1 = -1.27(0.07)\delta C_p + 286.5(8.4),\quad r = 0.97,\ s = 0.46. \qquad (4)$$

The principal causes of the influence of X on the benzene ring are the field and resonance effects,[41] which have been described most fully for various substituted benzenes in terms of resonance (R) and field (F) constants.[58] The difference between the values of δC for the *para*- and *meta*-positions in the ring of X−Ph is usually determined by the pure resonance effect of the group X.[59] In our case, the corresponding equation is

$$\delta C_p - \delta C_m = 0.22(0.09) + 4.7(0.3)F + 4.9(0.5)R,\quad r = 0.987,\ s = 0.2,\ n = 14. \qquad (5)$$

Consequently the field effect is the principal factor governing the influence of the groups X on the aromatic fragment through the triple bond. Examination of the shielding of the proton at the β-carbon atom of the triple bond in the *para*-substituted phenylactylenes $X-C_6H_4-C_\alpha\equiv C_\beta-H$, carried out by Klasine et al.,[29] leads to a similar conclusion.

The ability of the −C≡C− bridging group to transmit the influence of substituents can be estimated by comparing the values of δC_p for the compounds Ph−X, Ph−CH=CHX (*trans*-isomer), and Ph−C≡CX. The regression equations are presented below (the values of δC_p are quoted relative to the corresponding unsubstituted compounds with X = H). For monosubstituted benzenes, the values of δC_p were taken from Ewing[60] and those for *trans*-styrenes were taken from Glukhikh et al.[61]

$$\delta C_p(PhC\equiv CX) = 0.55(0.02)\delta C_p(PhX) + 0.75(0.18),\quad r = 0.98,\ s = 0.8,\ n = 29; \qquad (6a)$$
$$\delta C_p(PhCH=CHX) = 0.88(0.04)\delta C_p(PhC\equiv CX) - 0.19(0.09),\quad r = 0.99,\ s = 0.2,\ n = 11. \qquad (6b)$$

The transmission coefficient in Eqn. (6a) is identical with the value determined as a result of the investigation of the reactivities of dinuclear bridged systems (see, for example, Litvinenko, et al.[62]). It follows from Eqn. (6b) that the coefficient of the transmission of substituent effects to the benzene ring through the triple bond is close to the corresponding value for the double bond. The high confidence level of Eqn. (6b) can serve as evidence for the similarity of the formal mechanisms of the transmission of the substituent effect through the double and triple carbon−carbon bonds.

5. Characteristic features of the influence of substituents on the shielding of C_{sp}

Group IVA elements. The nature of the influence of substituents on the shielding of *sp*-carbon atoms in acetylenic compounds can be usefully examined by comparing the experimental values of δC_{sp} for acetylene itself and for its monosubstituted derivatives or by analysing the additive contributions found (Table 1). The characteristic features of the effects of alkyl groups on δC_{sp} can be seen from the comparison of the corresponding data for substituted acetylenes, ethanes,[63] ethylenes,[64,65] and benzenes[60,66] (the values of δC for the carbon atoms in these compounds are presented in Table 5).

A good relation is observed between the values of δC in the series of alkylacetylenes and alkylethylenes, the shielding of C_α in the series of alkyl-acetylenes being less sensitive (approximately by 30%) to the nature of the alkyl substituent than in the series of alkylethylenes.[67] The values of δC_{sp} for the β-carbon atoms in alkyl acetylenes remain virtually constant within the series. This is also characteristic of the C_p atoms of the benzene ring and reflects the independence of the π-polarisation of the unsaturated fragment of the size of the alkyl group. The increase in the shielding of the C_β atoms in ethynyl and vinyl derivatives and of the C_o atoms in phenyl derivatives is a consequence of the enhancement of the steric interaction of these atoms with the alkyl group as the bulk of the latter increases.

Substituents containing other Group IVA atoms influence the ethynyl fragment of the substituent quite differently. Since the effects of the $EAlk_3$ groups depend little on the character of E (Si, Ge, Sn) and of the alkyl (Alk), we shall examine them in relation to only the $SiEt_3$ group. The values of δC for hydrocarbon fragments

containing the $SiEt_3$ substituent (data taken from Proidakov[74]) are presented in Table 5. The deshielding effect of the $EAlk_3$ group on the C_β atom of the triple bond is stronger than for a single bond (by a factor of 20) and a double bond (by a factor of 2.5), while the shielding of the C_α atom in all the unsaturated fragments is the same.[52] The enhanced π-acceptor properties of the Si, Ge, and Sn atoms in relation to the triple bond have been explained by their ability to participate in the interaction with both its π-systems.[68] The fact that $EAlk_3$ groups deshield the C_β (C_o) atoms of the unsaturated fragments and hardly affect C_p in the benzene ring makes it possible to exclude from consideration the mechanism in which the effect is exerted through π-polarisation and through $p_\pi - d_\pi$ conjugation. Since the $EAlk_3$ groups act predominantly on the two nearest unsaturated carbon atoms, one can assume that the atomic orbitals of the two nearest sp^2- and sp-carbon atoms participate in the formation of the molecular orbitals (MO) responsible for the charge transfer from the π-system of the substituent to the atom E, which agrees with the model postulating the participation of the unoccupied σ* orbitals of the E–C bonds in the donor–acceptor interaction.[68]

Table 5. The ^{13}C chemical shifts (p.p.m. relative to TMS) of substituted ethanes, ethylenes, acetylenes, and benzenes.

R	$R-C_\alpha H_2-C_\beta H_3$		$R-C_\alpha H=C_\beta H_2$		$R-C_\alpha \equiv C_\beta H$	
	C_α	C_β	C_α	C_β	C_α	C_β
H	5.7	5.7	122.8	122.8	72.0	72.0
Me	15.9	15.4	136.2	115.9	79.3	67.0
Et	24.8	13.0	140.2	113.3	85.0	67.3
Pr^i	31.6	11.3	146.0	111.3	89.3	67.7
Bu^t	36.5	8.5	149.3	109.3	92.1	67.0
Et_3Si	2.8	6.9	137.8	132.6	86.2	95.4

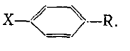
R	$R-C_6H_5$			
	C_1	C_o	C_m	C_p
H	128.5	128.5	128.5	128.5
Me	137.8	129.3	128.5	125.6
Et	144.1	128.1	128.5	125.9
Pr^i	148.7	126.6	128.6	126.1
Bu^t	149.1	125.4	128.4	125.9
Et_3Si	140.4	133.6	128.6	128.7

Group VIA and VIIA elements. Alkoxy- and aryloxy-groups significantly shield the C_β atom at the triple bond, displacing its signal by 20–30 p.p.m. relative to that of the TMS carbon atom,[20,21,69] which is explained by the effective conjugation of the lone electron pairs (LEP) of the oxygen atom with the π-electron system of the triple bond, i.e. with the appreciable contribution of the canonical structure of the type $R-\overset{\oplus}{O}=C=\overset{\ominus}{C}H$. The extent of such interaction has been examined in relation to ethynyl ethers.[69] The shielding of the C_β atom in the ether $PhOC_\alpha \equiv C_\beta H$ is less pronounced than in the ether $EtOC_\alpha \equiv C_\beta H$ (the difference between the displacements is 10 p.p.m.) in view of the competing interaction of two π-electron substituents with the ether oxygen as the electron donor. This is confirmed by the comparison of the values of δC of the phenyl group (p.p.m. relative to δC_{TMS}) for isoelectronic ethers R–O–Ph:

R	C_1	C_o	C_m	C_p
CH_3-CH_2	159.26	114.53	129.38	120.57
$CH_2=CH$	156.25	117.03	129.24	122.67
$CH \equiv C$	155.54	114.81	129.36	124.23

Comparison of the degrees of shielding of C_p in these compounds shows that the delocalisation of the charge of the oxygen LEP over the benzene ring diminishes by a factor of 1.4 on passing from the vinyl to the ethynyl ether and by a factor of 2 on passing from the ethyl to the ethynyl ether§, i.e. the degree of charge transfer from the oxygen atom to the triple bond is appreciably greater than the charge transfer to the double bond. This follows from a comparison of the excess shielding of the C_β atom in the ethynyl group (the displacement of the shift is by 38.4 p.p.m. relative to acetylene) and in the vinyl group (the displacement is by 28.2 p.p.m. relative to ethylene).[69] Bearing in mind the different sensitivities of the shielding of the C_{sp} and C_{sp^2} atoms to changes in their charge density,[29] one may conclude that the excess charge on the C_β atom in the ethynyl ether is greater by a factor of 1.6 than in the vinyl ether. The similarity of the excess charge follows from the results in the literature[33,50] subject to the condition that in acetylenic ethers both orthogonal π orbitals of the triple bond participate in the p_π interaction with oxygen. These results agree with the results of the calculation of the charge distribution in the hypothetical $HC \equiv COH$ and $H_2C \equiv CHOH$ molecules by the OST-3G method.[70]

The sensitivities of the chemical shifts of the C_p atom of the benzene ring and of the C_β atom of the multiple bond of the group R to the effects of the substituent X in the compounds



have been compared for *para*-substituted ethynyl phenyl,[69] phenyl vinyl,[23] and phenyl propargyl[71] ethers, substituted styrenes,[72] and phenylacetylenes.[29] It is seen from the data in Table 6 that the ΔC_p for these series of compounds are fairly close, in contrast to ΔC_β. The ratio $\Delta C_\beta / \Delta C_p$ is appreciably lower for ethynyl and especially propargyl ethers. The numbers presented in the last two columns of Table 6 indicate a decrease of the resonance effect in the case of substituted acetylenes, while the field effect, i.e. the π-induction effect, remains unchanged. As was to be expected, it becomes dominant in propargyl ethers. This is also confirmed by the relation between δC for *para*-substituted propargyl ethers $CH \equiv CCH_2O-C_6H_4X$ and the dipole moments[73] of the corresponding monosubstituted benzene derivatives Ph–X:

$$\delta C_\beta = 0.34\,(0.04)\,\mu_{PhX}, \quad r = 0.975,\ s = 0.14,\ n = 7. \qquad (7)$$

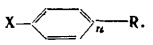
§ The charge transfer from the ether oxygen atom to the benzene ring can be most correctly estimated from the change in δC_p (this value is proportional to the change in the charge on the atom):

	δC_p, p.p.m.	$\Delta\delta C_p$, p.p.m. (relative to benzene)
C_6H_6	128.5	0
$C_2H_5OC_6H_5$	120.4	−8.1
$CH_2=CHOC_6H_5$	122.7	−5.8
$CH \equiv COC_6H_5$	124.2	−4.3

i.e. the charge transfer to the benzene ring on passing from the ethyl to the vinyl ether diminishes by a factor of (−8.1/−5.8) ≃ 1.4 whilst on passing from the ethyl to the ethynyl ether the decrease is by a factor of (−8.1/−4.3) ≃ 2.

Thus the influence of substituents capable of conjugation on the shielding of the carbon atoms of the triple bond through the saturated fragment is exerted via its π-polarisation.

Table 6. The displacements of the chemical shifts of the C_p atom of the benzene ring and the C_β atom of the multiple bond (in p.p.m.) and their sensitivity to the effects of the substituent X in the compounds



R	ΔC_n	ΔC_β	$\Delta C_\beta/\Delta C_n$	$\lambda(C_n)$	$\lambda(C_\beta)$	$\rho_R(C_\beta)/\rho_R(C_n)$	$\rho_F(C_\beta)/\rho_F(C_n)$
CH_2=CH	13.1	7.0	0.54	6.8	2.6	0.45	1.03
CH≡C	13.8	6.1	0.44	6.4	1.8	0.28	0.98
CH_2=CHO	10.6	5.5	0.52	6.9	1.9	0.32	1.17
CH≡CO	10.0	2.9	0.29	8.8	1.7	0.20	1.00
CH≡CCH_2O	11.2	1.6	0.14	6.1	1.0	0.08	0.45

Note. ΔC is the range of variation of δC when X is varied in the series from the NO_2 acceptor to the OMe donor; $\lambda = \rho_R/\rho_F$ is the ratio of the sensitivities of δC to the resonance and field effects obtained from statistically reliable correlations ($r \geqslant 0.99$).

Table 7. The influence of the heteroatomic groups Alk_nE on the shielding of α- and β-carbon atoms of substituted acetylene, benzene, and ethane derivatives (displacements of the chemical shifts, p.p.m.).[78]

n	E	Electro-negativity E*	$Alk_nE-C\equiv CH$		Alk_nE-Ph		Alk_nE-Et	
			δC_α	δC_β	δC_α	δC_β	δC_α	δC_β
3	C	2.50	19.9	—5.0	22.5	—3.2	—	—
	Si	1.74	17.3	21.7	11.7	4.9	—1.1	1.7
	Ge	2.02	17.2	20.3	13.7	4.5	0.1	3.2
	Sn	1.72	17.3	24.3	13.4	7.4	—3.4	5.1
	Δ **	—0.02	0.0	2.6	1.7	2.5	—2.3	3.4
1	O	3.50	22.1	—50.9	31.3	—14.0	57.3	9.2
	S	2.44	2.4	8.9	8.4	0.1	21.5	8.7
	Se	2.48	—8.2	14.9	1.9	3.8	15.2	9.7
	Te	2.01	—34.3	27.0	—16.5	9.6	—6.1	10.5
	Δ **	—0.43	—36.7	18.1	—24.9	9.7	—27.6	1.8
0	F	4.10	—	—	35.3	—13.9	63.6	8.9
	Cl	2.83	—11.1	—14.7	6.6	—1.6	34.2	13.0
	Br	2.74	—29.4	—3.7	—5.2	3.5	20.6	14.6
	I	2.21	—71.1	13.3	—13.8	10.4	—5.5	15.9
	Δ **	—0.62	—60.0	28.0	—38.4	12.0	—39.7	2.9

Note. The displacements of the chemical shifts are quoted relative to the corresponding unsubstituted compounds.

* The electronegativities of the heteroatoms taken from Batsanov[77] are quoted.

** The differences between the corresponding values obtained on passing from elements of the 3rd Period to those of the 5th Period are quoted.

The results presented characterise the ability of bridging groups to transmit the electronic effects and show that the employment of "transmission factors" for individual bridging groups as stable characteristics is erroneous.[62] Comparison of the values of $\Delta C_\beta/\Delta C_p$ for the first four compounds demonstrates that the ability of the ether oxygen to transmit perturbations is significantly different even in fairly close structural series and depends on the conformational structure of the molecules, the character of the detector group, and, finally, on the property or parameter of the group chosen for the comparison. The ether oxygen atom has an enhanced π-donor capacity in relation to the triple bond because it can interact simultaneously with two orthogonal π orbitals. This is reflected in the non-universality of the existing scales of the resonance constants σ_R (with the possible exception of Katritzky's scale[33,50] mentioned above), which is due to the unequal effectiveness of the interaction of the group R with different (as regards the character of the symmetry of the π-system) unsaturated fragments. In the compounds $AlkEC_\alpha\equiv C_\beta R$, where E = S, Se, or Te, an increased shielding is characteristic of the C_α atoms (regardless of the character of R); the chemical shift is displaced by 9—11 p.p.m. on passing from the sulphides to the selenides and by 33—36 p.p.m. on passing from the sulphides to the tellurides. On the other hand, the C atom is deshielded and the corresponding displacements are 5—6 and 17—18 p.p.m.[53] Evidently chalcogens exhibit π-acceptor properties in relation to the triple bond, because the EtS and $EtCH_2$ groups, having similar induction constants, exhibit significantly different effects on the vinyl and ethynyl fragments, while the effects on the ethyl groups are similar (the values of δC are listed below in p.p.m.):[74]

	$R-C_\alpha H_2-C_\beta H_3$		$R-C_\alpha H=C_\beta H_2$		$R-C_\alpha\equiv C_\beta H$	
	C_α	C_β	C_α	C_β	C_α	C_β
δC(R=EtS)	26.5	15.8	132.7	109.7	74.0	82.2
δC(R=$EtCH_2$)	22.6	13.7	137.6	113.5	83.6	68.2
Δδ C	3.9	2.1	—4.9	—3.8	—9.6	14.0

Whereas the π-electronic effect of the ethylthio-group on the C_β atom of the double bond is shielding, in the case of the triple bond it has the opposite sign and is three times greater. It may be that in the latter case this effect has the character of $d_\pi-p_\pi$ conjugation. Such conjugation is promoted by the increase in the electronegativity of the substituent at the sulphide sulphur atom.[68,75] This is confirmed by the X-ray fluorescence spectra of the compounds $AlkEt\equiv CH$, which indicate an appreciable contribution of the charge on the 3*d* orbitals of the sulphur atom.[76] A non-empirical calculation for the $HSC\equiv CH$ molecule in terms of the contracted STO-3G basis set[70] indicates nevertheless the existence of an appreciable negative charge (−0.19) on the ethynyl fragment. On the basis of the concept of the π-acceptor nature of the deshielding of the C_β atom, one may conclude that, since it increases significantly from sulphur to tellurium, the $5d-2p$ π-interaction is energetically most favourable. In view of the unexpected nature of this conclusion, we shall consider the characteristic features of the influence of Group VIA elements on the δC of the closest carbon atoms of the group R in the series of isologous compounds of Group IVA, VIA, and VIIA elements (Table 7). With increase in the number of the Period, the shielding of the C_{sp^2} atom, in the α-position relative to the Group VIA element, leads to an increase in the chemical shift by 50—70 p.p.m., while δC_β hardly changes. In the series of halogenoalkanes, the character of the changes in δC is analogous, although their range is wider by 20—30%.[79,80] In the isologous series of compounds of Group IVA elements (Alk_3ER), the changes in δC for the alkyl group are not regular and their range is much narrower.[81]

The shielding effect of the chalcogens on C_α in the case of sp^2-carbon atoms increases with increase in the number of the Period, as for sp^3-carbon atoms, although the range of variation of

δC in the latter case is somewhat wider. The values of δC_β for the C_{sp^2} atoms increase with increase in the atomic number of E and for the vinyl fragment this increase is more appreciable than for the phenyl fragment (Table 7). This is apparently induced by the redistribution of the π-charge of the heteroatom in the case of the phenyl substituent between two positions (*ortho*- and *para*-positions).[78]

The shift δC_{sp} changes under the influence of the heteroatom E (E = O, S, Se, Te) approximately in the same way as in halogenoacetylenes, but the change is different from that observed in Group IVA elements (Table 7).

In the isologous series of compounds of Group IVA, VIA, and VIIA elements (Table 7), the "heavy atom effect" apparently makes a considerable contribution to the change in the shielding of the C_α and C_β atoms of the triple bond in the chalcogenides and halides. The occurrence of this effect for the halogens has been noted in a number of studies.[80,82,83] Although the electronegativity of Group IVA elements also changes appreciably, this effect is not manifested in this instance. The following qualitative model of the observed phenomenon can be proposed. The effect of the elements of different Groups in the Periodic System on neighbouring hydrocarbon fragments is determined by the presence in these elements of different numbers of LEP (O for C, Si, Ge, Sn, and Pb, 2 for O, S, Se, and Te, and 3 for F, Cl, Br, and I), which are capable of interacting with substituents at a distance more strongly the greater the increase of the diffuseness of the corresponding *p* orbitals within the Group. The size of the substituent, the presence in the latter of a π-system, and the polarisability of the system determine the extent of the influence of the heteroatom on the substituent, i.e. the extent of the changes in δC. The absence of the "heavy atom effect" in Group IVA elements is a consequence of the absence of the LEP from them.

Since a rigorous test of this concept by a reliable quantum-chemical calculation of the shielding of the ^{13}C nuclei for the set of compounds examined has not been carried out, the results are mainly of applied interest—they assist in the correct assignment of the ^{13}C signals.

III. The constants for the spin–spin coupling in the acetylenic fragment

For all acetylenes without exception, it is possible to measure only one spin–spin coupling constant $^1J_{CC}$. In addition, for monosubstituted acetylenes it is possible to measure the SSCC between the terminal proton and the acetylenic carbon atoms across one and two bonds: $^1J_{CH}$ and $^2J_{CH}$ respectively.

1. The spin–spin coupling constants $^1J_{CH}$ and $^2J_{CH}$

The values of the SSCC $^1J_{CH}$ and $^2J_{CH}$ for acetylene (these constants have been measured most accurately by Mohantry[84]) are +248.97 and +49.62 Hz respectively. The SSCC for more than 60 monosubstituted acetylenes are presented in Table 8. The range of variation of $^1J_{CH}$ is about 50 Hz and that of $^2J_{CH}$ is about 25 Hz. For the series of compounds HC≡CX, a relation has been obtained from which it follows that the electronegativity X exerts a decisive influence on $^1J_{CH}$:[88]

$$^1J_{CH} = 208.4\,(4,7) + 17.4\,(1.8)\,E_X,\ r = 0,95,\ n = 13. \quad (8)$$

The following relation has also been put forward:[89]

$$^1J_{CH} = 5,7\,(\%s) - 18,4, \quad (9)$$

It has been used to estimate the amount of *s* character of the carbon atom in discussing the mechanisms of the interaction of various heteroatomic substituents with the triple bond.[20,21] The appreciable decrease of these SSCC for compounds containing Si, Ge, or Sn atoms as substituents at the triple bond has been explained in a number of publications[3,7,8,90] by the decrease in the amount of *s* character of the hybrid orbital of the terminal carbon atom, participating in the formation of the C–H bond, as a result of the π=acceptor effect of E: $R_3\overset{\ominus}{E}=C=\overset{\oplus}{C}-H$. This model is relatively unconvincing because $d_\pi - p_\pi$ interaction is also characteristic of the substituents R_2SO_2 (this follows from the appreciable population of the *d* orbitals of the sulphur atom according to X-ray fluorescence data), although for these compounds $^1J_{CH}$ is greater by 13 Hz than for alkynes (Table 8). Furthermore, the decrease in the amount of *s* character of the terminal carbon orbital in ethynyl ethers can be induced by the π-donor properties of oxygen:

$$RO-C\equiv C-H \longleftrightarrow \overset{\oplus}{RO}=C=\overset{\ominus}{C}-H.$$

However, in this case too there is an appreciable increase in $^1J_{CH}$ and the influence of the nature of R on $^1J_{CH}$ is insignificant (Table 8).

Table 8. The spin–spin coupling constants $^1J_{CH}$ and $^2J_{CH}$ (in Hz) for monosubstituted acetylene derivatives R–C≡CH.

R	$^1J_{CH}$	$^2J_{CH}$	Refs.	R	$^1J_{CH}$	$^2J_{CH}$	Refs.
H	249.0	49.6	[85]	$HOCH_2C\equiv C$	259.0	52.5	[41]
Me	247.6	50.8	[37]	N≡C	266.8	53.4	[41]
Bu	247.7	50.0	[86]	EtO	263	—	[21]
Hex	247.3	49.9	[86]	PhO	265.5	60.3	[41]
Bu^t	246.5	48.9	[86]	*p*-$MeOC_6H_4O$	265.5	59.5	[41]
$(CH_2)_5C(OH)$	248.7	49.0	[86]	*p*-MeC_6H_4O	265.3	59.3	[41]
$HOCH_2$	251.3	50.0	[86]	*p*-ClC_6H_4O	266.0	59.7	[41]
$PhOCH_2$	251.5	50.7	[86]	*p*-$NO_2C_6H_4O$	269.1	60.9	[41]
o-$NO_2C_6H_4OCH_2$	253.0	50.0	[86]	EtS	253	—	[21]
p-$NO_2C_6H_4OCH_2$	254.2	50.9	[41]	PhS	256	51.6	[87]
p-$C_6H_4OCH_2$	251.5	50,6	[41]	$BuSO_2$	266	—	[21]
p-$BrC_6H_4OCH_2$	252.0	50.0	[41]	Me(Ph)N	258	—	[21]
p-$FC_6H_4OCH_2$	251.3	49.8	[41]	Ph_2N	259	55.5	[21]
p-$MeC_6H_4OCH_2$	251.5	49.9	[41]	Pr_3^iP	244	45	[41]
p-$MeOC_6H_4OCH_2$	251.5	49.9	[41]	Bu_2^tP	246	46	[41]
$CCl_2=CHOCH_2$	252.9	50.3	[41]	Ph_2P	247	45.8	[87]
$(CCl_2=CHOCH_2)_2$	250.8	49.5	[41]	Bu_3^tPO	252	49	[21]
$BrCH_2$	252.4	49.3	[86]	$Pr^iP(S)$	250	46	[41]
$ClCH_2$	252.6	50.5	[86]	Me_3Si	236.8	42.2	[86]
$PhCH_2$	251.0	49.7	[86]	Et_3Si	236.8	42.3	[86]
$MeOCH_2$	253	49	[41]	Cl_3Si	249.1	44.0	[86]
Ph_3SiCH_2	247.1	50.0	[87]	Ph_3Si	241.2	41.2	[9]
$(CH_2)_4NCH_2$	247.9	49.5	[41]	Me_3Ge	236.0	42.0	[41]
$(CH_2)_5NCH_2$	248.2	48.9	[41]	Et_3Ge	235.7	41.9	[86]
$(CH_2)_6NCH_2$	247.3	48.5	[41]	Cl_3Ge	253.1	45.9	[86]
$O(CH_2)_4NCH_2$	248.8	49.7	[41]	Ph_3Ge	238.2	41.2	[9]
$CH_2=CH$	251.1	50.1	[41]	Et_3Sn	232.6	41.3	[86]
Ph	250.6	49.1	[41]	Ph_3Sn	238	41	[41]
HC≡C	257.3	52.6	[41]	F	277.5	65.5	[88]
MeC≡C	257.3	52.4	[41]	Cl	270	60.5	[88]
$Bu^tC\equiv C$	256.6	50.6	[41]	Br	261	56.0	[88]
PhC≡C	256.9	51.6	[41]	I	255	51.5	[88]
				COOH	259.3	50.1	[41]

A reliable relation between $^1J_{CH}$ for monosubstituted acetylenes and characteristics of the substituents (σ_I, σ_R, *F*, *R*) other than E_X could not be observed, although the correlation between the constants $^1J_{CH}$ and $^2J_{CH}$ is reliable:[41]

$$^1J_{CH} = 1,73\,(0,07)\,^2J_{CH} + 164\,(3.5),$$
$$r = 0.975,\ s = 2.0,\ n = 35. \quad (10)$$

The latter shows that both these SSCC are controlled by the same factors.

2. The spin–spin coupling constants $^1J_{CC}$

The values of $^1J_{CC}$ increase sharply with increase in the *s* bond order: in the calculation by the method involving summation with respect to states in terms of the "average excitation energy" approximation, the Fermi-contact contribution is proportional to the product of the amounts of *s* character of the hybrid orbitals of the interacting carbon atoms forming the C–C bond.[91] In acetylenic compounds, the *s* order has the maximum possible value (50%), which is the reason for the very high values of $^1J_{CC}$ and the wide range of their variation.

For acetylenic compounds, the constants $^1J_{CC}$ increase linearly, like the constant $^1J_{CH}$, with increase in the electronegativity of the substituent,[86,92,93] which is induced by the increase in the Fermi-contact contribution.[94] A specific feature of the $^1J_{CC}$ for acetylenic compounds is a significant contribution of non-contact interactions transmitted predominantly via the π-electron system.[95]

The range of the experimental values of $^1J_{CC}$ (for 100 acetylenic compounds[96]) is unusually large: from 56.8 to 230.4 Hz, i.e. more than 170 Hz. According to theoretical estimates,[97] the limiting values may be 31.8 Hz (LiC≡CLi) and 356.0 Hz (FC≡CF). If the group electronegativity parameter of the substituent σ^2, calculated from the atomic charge density of hydrogen in the H–X molecules by the *ab initio* method in terms of the 6-31GF basis set[98] disregarding π-interactions, is used as a characteristic of the substituent in monosubstituted acetylenes, it is possible to obtain the relation

$$^1J_{CC} = 317.6\,(11.9)\,\sigma_\chi^2 + 164.9\,(0,8),$$
$$r = 0.983,\ s = 4.0,\ n = 27. \qquad (11)$$

Equations of a similar type have also been found for disubstituted acetylenes with a single fixed substituent, although this approach does not take into account the mutual influence of the substituents, which leads to non-additivity. A general relation for all acetylenic compounds of the type XC≡CY assumes the form[96]

$$^1J_{CC} = 270.8\,(7.3)\,(\sigma_\chi^2 X + \sigma_\chi^2 Y) + 720.4\,(151.8)\,\sigma_\chi^2 X \sigma_\chi^2 Y + 162.4\,(0.7),$$
$$r = 0.982,\ s = 5.4,\ n = 59. \qquad (12)$$

The cross-term in Eqn. (12), which is statistically significant, reflects the non-additivity of the influence of the substituents. It is greatest when the α-atom of one of the substituents is Si, Ge, Sn, Br, I, or Hg, which influences significantly the π-system of the acetylenic compound.

There is a reliable relation between the constant $^1J_{CC}$, on the one hand, and $^1J_{CH}$ and $^2J_{CH}$ for monosubstituted acetylenes:[96]

$$^1J_{CC} = 2.87\,(0.15)\,^1J_{CH} - 545.6\,(37.1),$$
$$r = 0.981,\ s = 4.37,\ n = 16; \qquad (13a)$$
$$^1J_{CC} = 5.67\,(0.25)\,^2J_{CH} - 109.6\,(12.0),$$
$$r = 0.986,\ s = 3.70,\ n = 17. \qquad (13b)$$

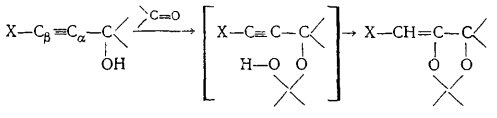
The statistically significant (r = 0.995) relation between the constants $^1J_{CC}$ for disubstituted acetylenes and the force constants of the triple bonds in these compounds must be regarded as the most reliable relation for practical purposes.[99]

IV. Relation between the reactivity of substituted acetylenes and the chemical shifts of the ethynyl carbon atoms

The reactivity of acetylenic compounds and the stereospecificity of the addition of various reactants to them depend on the nature of the substituents, which determine the energy of the transition state, the steric accessibility of the triple bond to the attack by reactants, and the distribution of electron density in the molecule.

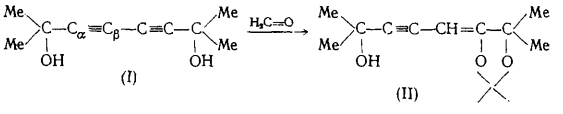
Since, according to literature data,[20,21] the values of δC_{sp} on the ^{13}C NMR spectra reflect the distribution of electron density in the acetylenic fragment, the difference between them ($\Delta\delta C$) characterises the polarisation of the triple bond. Presumably, these parameters can have a definite importance for the explanation and prediction of the regiospecificities and stereospecificities of reactions involving addition to the triple bond and in general as regards the possibility of their occurrence. The search for such relations is the aspect of the application of NMR to acetylene chemistry of greatest current interest.

The reaction involving the addition of carbonyl compounds to α-ethynyl alcohols containing a wide range of functional groups, both directly at the triple bond and separated from them by the methylene bridge, has been studied:[49,100–107]



Heterocyclisation proceeds readily in the series of α-ethynyl alcohols with X = Br, CN, COOR, COR, or C≡CR, but does not occur when X = H, CH=CH$_2$, PhO, ROCH$_2$, or R$_2$NCH$_2$. This difference in the chemical behaviour agrees well with the parameters of the ^{13}C NMR spectra of the corresponding acetylenic compounds.[49,100] Thus, whereas $\Delta\delta C_{\alpha,\beta}$ for the terminal alcohols (X = H) is 8–19 p.p.m., for the bromo-derivatives (X = Br) this quantity reaches 32–42 p.p.m., i.e. in the halogenoalcohols the degree of polarisation of the triple bond is greater, which favours nucleophilic addition. The direction of polarisation is determined mainly by the σ-acceptor effect of the bromine atom.

It is of interest to note that formaldehyde interacts with only one hydroxyethynyl group of the diacetylenic glycol (I):



Analysis of the values of δC for the dyne (I) and the enyne dioxolan (II) permits the conclusion that in the former case polarisation promotes the nucleophilic addition of the hydroxy-group with formation of the dioxolan ring, while in the latter case polarisation has the opposite direction and hinders the heterocyclisation ($\Delta\delta C_{\alpha,\beta}$ = 19.2 and –20.6 p.p.m. respectively[49]). In the isotypical compounds XCH$_2$C$_\beta$≡C$_\alpha$CH$_2$OH, in which the substituent X is separated from the triple bond by the methylene bridge, the changes in δC are determined mainly by its polar influence:[49]

$$\delta C_\alpha = 78.4\,(1.4) + 12.0\,(1.4)\,\sigma^*(XCH_2),\quad r = 0.977 \qquad (14)$$

The qualitative relation between $\Delta\delta C$ and the reactivity of substituted propargyl alcohols suggested an increase in the reactivity of substrates on passing from bases (aminoalcohols) to their quaternary

salts, for which the values of $\Delta\delta C$ are higher:[49]

$R_2NCH_2C_\beta{\equiv}C_\alpha C(OH)R^1R^2$ $\quad$ $I^{\ominus}MeR_2\overset{\oplus}{N}CH_2C_\beta{\equiv}C_\alpha C(OH)R^1R^2$

$\Delta\delta C_{\alpha,\beta}=4-7$ p.p.m. $\quad$ $\Delta\delta C_{\alpha,\beta}=17-22$ p.p.m.

The heterocyclisation of aminoalcohols on heating with paraformaldehyde in the presence of bases (potassium carbonate, potassium hydroxide, tetraethylammonium hydroxide) in boiling methanol for 8 h does not take place although the corresponding methiodides readily cyclise even at room temperature, affording high yields (75–90%) of the methiodides or 4-(2-dialkylaminoethylidene)-1,3-dioxolans. The latter were also obtained from the methiodides (IIIa–c) and the reactivity of these salts also agrees with the differences in δC_{sp}:[101]

$$I^{\ominus}MeR_2\overset{\oplus}{N}CH_2C{\equiv}CH \xrightarrow[KOH-EtOH]{H_2C=O} \overset{\ominus}{I}MeR_2\overset{\oplus}{N}CH_2CH{=}C(CH_2)(O)(O)(CH_2)$$

(IIIa–c) $\quad$ (IVa–c)

R = Me (a), Et (b), C_5H_{10} (c).

Comparison of the parameters of the ^{13}C NMR spectra of propargylamines $R_2NCH_2C_\beta{\equiv}C_\alpha H$ ($\Delta\delta C_{\alpha,\beta}$ = –5–6 p.p.m.) and their salts ($\Delta\delta C_{\alpha,\beta}$ = 8–12 p.p.m.)[101] permits the assumption that the triple bond in the molecules of the salts is polarised by the σ-acceptor effect of the ammonium group, which increases the acidity of the acetylenic proton and facilitates the interaction with paraformaldehyde under the conditions of the Favorskii reaction. This hypothesis has been confirmed by experimental data: on interaction with paraformaldehyde in alcoholic potassium hydroxide solution (60 °C, 1 h), the methiodides readily form substituted 1,3-dioxolans (IVa–c) in 90–91% yield.[101]

Terminal α-ethynyl alcohols react with phenyl isocyanate to form the corresponding *N*-phenylcarbamates, which isomerise to 4-alkylidene-2-oxazolidinones in the presence of bases:[108–110]

$$H{-}C{\equiv}C{-}CR_2(OH) \xrightarrow{PhNCO} H{-}C{\equiv}C{-}CR_2(NH{-}Ph)(C{=}O) \rightarrow CH_2{=}C(CR_2)(N(Ph)(C{=}O))(C{=}O)$$

Substituted 4-dialkylaminobut-2-yn-1-ols (V) also react with phenyl isocyanate to form the corresponding *N*-phenylcarbamates (VI), but their cyclisation in the presence of bases to the corresponding 2-oxazolidines does not occur:[111]

$$R_2NCH_2C_\beta{\equiv}C_\alpha{-}CR'_2(OH) \xrightarrow{PhNCO} R_2NCH_2C{\equiv}C{-}CR'_2(O)(C(=O)NHPh) \longrightarrow$$

(V) $\quad$ (VI)

$$\rightarrow \overset{\ominus}{I}MeR_2\overset{\oplus}{N}CH_2C{\equiv}CCR'_2(O)(C(=O)NHPh) \rightarrow \overset{\ominus}{I}MeR_2\overset{\oplus}{N}CH_2CH{=}C(CR'_2)(N(Ph)(C{=}O))(O)$$

(VII) $\quad$ (VIII)

R, R′ = Alk

This difference between the reactivities of the carbamates of terminal ethynyl alcohols[108–110] and their aminomethyl analogues can be explained on the basis of ^{13}C NMR spectroscopic data. The polarisation of the triple bond is essential for the nucleophilic attack by the nitrogen atom on the ethynyl carbon atom. The electron-donating substituents R_2NCH_2 give rise to an unfavourable polarisation: $\Delta\delta C_{\alpha,\beta}$ = 0–7 p.p.m. For the methiodides (VII), $\Delta\delta C_{\alpha,\beta}$ = 10–15 p.p.m., i.e. a deficiency of electron density arises on the C_α atom, creating favourable conditions for nucleophilic attack. Indeed, in the presence of sodium methoxide at room temperature, the methiodides (VII) cyclise to the oxazolidines (VIII) in high yields.[111]

The set of data obtained for aminoalkyl- and bromo-ethynyl alcohols in the heterocyclisation reaction justifies the hypothesis that the polar and not the steric influence of the substituents at the ethynyl carbon atom is the decisive factor for its occurrence.

Thus, according to the available data, for the reaction involving addition to the ethynyl alcohols there is a qualitative correspondence between the reactivity and the ^{13}C chemical shifts of the initial acetylenic compounds, although the values of δC_{sp} themselves cannot serve as an adequate criterion of the charge distribution on the triple bond.

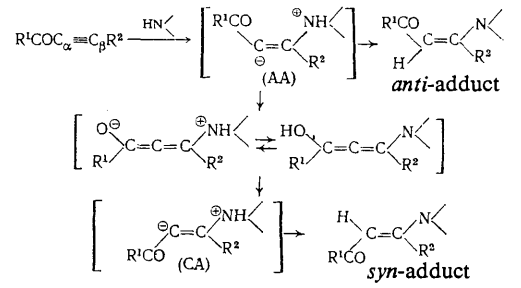
The results of a kinetic study of the hydroboration reaction of 1-halogenoalk-1-ynes, which is important for synthesis, have shown[112] that the rate of reaction and its regioselectivity agree with the parameters of the ^{13}C NMR spectra.

The addition of nucleophiles to α-ethynyl ketones is an important and widely occurring reaction. The conjugation of the triple bond with the carbonyl group ($-C^4{=}C^3{-}C^2{=}O^1$) permits 1,2-, 3,4-, and 1,4-addition. Thus alcohols and amines add to the 3,4-positions, while hydrazines and semicarbazides add to the 1,2-positions. Hydroxylamines, which occupy an intermediate position as regards nucleophilicity between strong (hydrazines) and weak (amines, alcohols) nucleophiles, react with both electrophilic centres simultaneously.[113] However, there is no rigorous correlation between the basicity of the amines and the reactivity of acetylenic ketones.[114,115] The relation between the reactivity of acetylenic ketones and other parameters—the Hammett constants[114] and entropy characteristics,[116] including parameters of the ^{13}C NMR spectra[117,118]—have been investigated. NMR parameters serve as an extremely useful source of information, provided that δC_{sp} does indeed characterise the electron density on these compounds and the difference between them characterises the polarisation of the triple bond,[20,21] which determines the reactivity of acetylenes in nucleophilic addition reactions.

One of the first attempts on these lines involved the study of the reactivity α-ethynyl ketones in reactions with amines and the search for a relation between the reactivity of substrates and the characteristics of the ^{13}C NMR spectra.[117] If the variable substituents R^1 and R^2 are located directly at the ynone fragment ($R^1COC_\alpha{\equiv}C_\beta R_2$), when their anisotropic and steric effects on δC_{sp} are considerable, the changes in δC_{sp} do not reflect the true changes in electron density on the C_α and C_β atoms, and the values of $\Delta\delta C_{\alpha,\beta}$ are not related to the corresponding kinetic parameters.[117,118] If the R^1 and R^2 substituents are remote from the triple bond in space (for example, in $R^1C_6H_4COC_\alpha{\equiv}C_\beta C_6H_4R^2$), then a relation between δC_{sp} and the electronic properties of the substituents is manifested. However, in this case too there is no linear relation between the rate constants for the addition of morpholine to these substances and $\Delta\delta C$.[41,74,118] The electron-donating substituents R^1 in the *para*-position in the benzene ring reduce both the reaction rate and $\Delta\delta C$, while electron-donating substituents R^2 reduce the reaction rate but increase $\Delta\delta C$ (Fig. 2). On the other hand, a satisfactory relation is observed between the reaction rate and the ratio of the products formed (Fig. 3).

Both the reaction rate and the yield of the *syn*-adduct increase with the enhancement of the electron-accepting character of the substituents. This is apparently associated with the fact that, in

conformity with the reaction mechanism established,[74] the probability of the isomerisation of the *anti*-anion, formed initially, to the *syn*-anion (SA) and hence also the fraction of the *syn*-adduct should increase as a result of the stabilisation of the intermediate by the electron-accepting substituents:



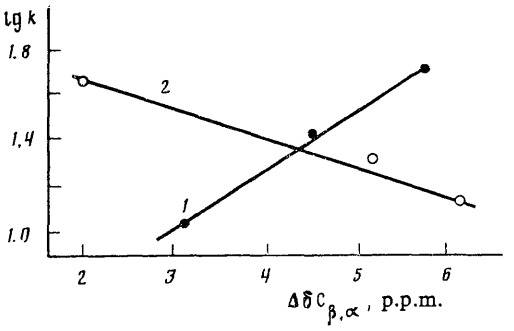


Figure 2. Dependence of the rate constants for the reactions between $R^1C_6H_4COC{\equiv}CC_6H_4R^2$ and



on $\Delta\delta C_{\beta,\alpha}$:[74] (1) variation of the substituents R^1; (2) variation of the substituents R^2.

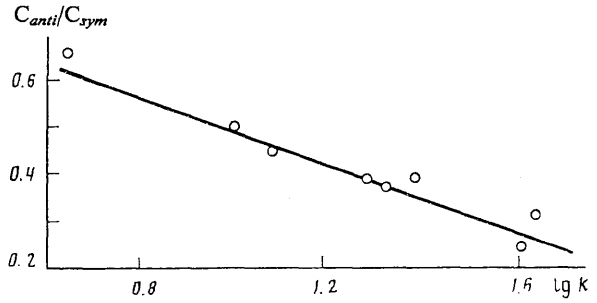


Figure 3. Dependence of the isomer ratio (determined from ^1H NMR spectra) on the reaction rate constant (lg *k*).[74]

It is also possible that the reaction rate and the ratio of the isomers are determined by the rate of protonation of the oxygen of the carbonyl group in the intermediate, which depends on the charge on the oxygen atom.[118]

A qualitative relation between the reactivity of acetylenes and the parameters of their ^{13}C NMR spectra has been noted in a number of studies. Thus the reactivity of thiacycloalkynes increases with increase in δC_{sp} (the polarisation of the triple bond).[119]

The site where nucleophiles are inserted into the acetylenic fragment of halogenoacetylenes cannot be predicted unambiguously, because it is known[120] that they contain three centres susceptible to nucleophilic attack: the halogen atom and the C_α and C_β carbon atoms of the triple bond. Under the conditions of the Arbuzov rearrangement, halogenoacetylenes react with trialkyl phosphites to form the products resulting from the substitution of the halogen (attack on C_α):[121,122]

$$RC_\beta{\equiv}C_\alpha X + P(OAlk)_3 \rightarrow [RC{\equiv}CP(OAlk)_3]^{\oplus}X^{\ominus} \rightarrow RC{\equiv}CP(O)(OAlk)_2 + AlkX.$$

Both the values of δC_{sp} (Table 9) and the distribution of the effective charges in model compounds calculated in terms of the CNDO/2 approximation agree with the experimental composition of the products.[122,126] The value of δC_α is lowest for the ynamine probably because of the strong π-donor effect of the dimethylamino-group in the "push-pull" system (a system with concerted effects of two substituents).

Table 9. The ^{13}C chemical shifts of the *sp* carbon atoms (in p.p.m. relative to TMS) and the differences between them ($\Delta\delta C$, p.p.m.) for certain heteroatomic substituted acetylenes $R^1C_\alpha{\equiv}C_\beta R^2$.

R^1	R^2	δC_α	δC_β	$\Delta\delta C_{\alpha,\beta}$	Refs.
$(MeO)_2P(O)$	Cl	54.04	75.88	−18.84	[121]
$(EtO)_2P(O)$	Cl	57.49	74.56	−17.07	[121]
$(MeO)_2P(O)$	Br	66.71	62.15	4.56	[121]
$(EtO)_2P(O)$	SEt	82.10	90.00	−7.90	[122]
$(EtO)_2P(O)$	SEt	86.15	93.71	−7.56	[123]
$(EtO)_2P(O)$	SPr	86.74	93.30	−6.56	[123]
$(EtO)_2P(O)$	SBu	85.87	92.68	−7.71	[123]
$Cl(PPh_3)$	SPh	76.97	112.30	−35.33	[123]
$(PrO)_2P(O)$	NMe_2	48 01	63.89	−14.88	[123]
Cl	SEt	69.57	59.71	9.81	[123]
Cl	SPr	68.65	59.71	8.94	[123]
$CH_2{=}CH$	SMe	91.38	82.20	9.18	[22]
$CH_2{=}CH$	SeMe	97.53	72.57	24.96	[22]
$CH_2{=}CH$	TeMe	109.66	49.48	60.18	[22]
$CH_2{=}CH$	H	78.4	82.5	−4.1	[124]
***cis*-MeCH=CH**	NEt_2	62.65	99.45	−36.80	[125]
***trans*-MeCH=CH**	NEt_2	63.50	98.75	−35.25	[125]
***cis*-MeCH=CH**	NPr_2	62.08	99.02	−36.94	[125]
$Me_2C{=}CH$	NPr_2	63.10	99.45	−36.35	[125]
$Me_2C{=}CH$	NEt_2	62.30	97.20	−34.90	[125]
H	OEt	23.4	89.6	−66.2	[21]
Me	OMe	28.2	88.6	−60.4	[21]
Et	OEt	35.7	87.8	−52.1	[21]

The preferential attack by the nucleophile on the carbon atom joined to the halogen atom occurs in the reaction of alkyl(aryl) chloroethynyl sulphides with triphenylphosphine and trialkyl phosphites. In the latter case, the only reaction products are the normal products of the Arbuzov rearrangement:[123]

$$(RSC{\equiv}\overset{\oplus}{C}PPh_3)Cl^{\ominus} \xleftarrow{PPh_3} RSC{\equiv}CCl \xrightarrow{P(OEt)_3} RSC{\equiv}CP(O)(OEt)_2.$$
(A) (B)

The signals of the C_α and C_β atoms in the ^{13}C NMR spectra of the reaction products (A) and (B) are deshielded relative to chloroacetylenes (Table 8) and the greatest degree of polarisation is observed in the ionic compound.

Organoelement compounds of the acetylenic series frequently exhibit a specific reactivity. An attempt has been made[11] to estimate the reactivity of silyl- and germyl-acetylenic carbonyl compounds from ^{13}C NMR data. Table 1 shows that the effects of the Si- and Ge-groups as well as carbonyl-containing groups are deshielding. Reactions of a silylacetylenic ketone with methyl- and dimethylamines proceed anomalously:

$$R_3SiC{\equiv}CC(O)Me + HNR^1R^2 \rightarrow R_3SiNR^1R^2 + R^2R^1N{-}CH{=}CHC(O)Me.$$

This unusual result has been explained[11] by the fact that the R_3E and C=O groups, which behave as acceptors in relation to the triple bond, diminish the electron density on both C_α and C_β atoms, which should reduce the reactivity of the triple bond in nucleophilic addition reactions. It is hardly possible to agree with this explanation. Electron-accepting groups are known to increase and not to decrease the reactivity of the triple bond in relation to nucleophiles. Thus it has been stated[113] that acetylenic compounds containing two electron-accepting substituents [the compounds PhC(O)C≡CC(O)Ph, PhC(O)C≡CC(O)Me, etc.] readily combine with amines at the triple bond. On the other hand, the result obtained by Arshavshkya et al.[11] is apparently associated with the fact that trialkylsilylacetylenes are very readily desilylated even at room temperature in the presence of a base,[127] whose role in the given reaction is probably assumed by the amine.

Alkynylamines and the related alkynyl ethers exhibit an unusual chemical reactivity, the reactivity of alkynyl ethers in ionic reactions being lower.[125,128]

The mode of addition of electrophiles and nucleophiles to alkenylamines[125] corresponds to their electronic structure, established by the CNDO/2 method, and the characteristics of their ^{13}C NMR spectra

$$\underset{-0.014}{cis\text{-}CH_3}-\underset{0.034}{CH}=\underset{-0.120}{CH}-\underset{0.061}{C_\alpha}\equiv C_\beta-\underset{-0.176}{N(C_2H_5)_2}$$

The excess electron density on the C_α atom agrees with the manifestation of the π-donor effects of nitrogen in the ^{13}C NMR spectra (Table 8). Although the values of δC_α for diethylamino- and dipropylamino-pent-3-en-1-ynes (62.65 and 62.08 p.p.m. respectively) as well as the values of δC_β for these compounds (99.45 and 99.02 p.p.m.) agree with the calculated charges, the upfield shift of the C_α signal and the value of $\Delta\delta C_{\alpha,\beta}$ for the alkynylamines are significantly smaller than might have been expected from data for the alkynyl ethers.[21] This indicates a more effective interaction of the ether oxygen with the π-systems of the triple bond,[41] but conflicts with experimental data according to which alkynylamines are much more reactive than alkynyl ethers in electrophilic addition reactions (attack on the C_α atom).[125] It has been suggested[125] that this is associated with the dynamic shift of the *p* electrons of the nitrogen atom towards the triple bond at the instant of reaction.

The regiospecificity of the addition of organocopper compounds to various heterosubstituted acetylenes is determined by the influence of the heteroatoms:[129]

$$\underset{\text{E=N, O, S.}}{\underset{\text{(IX)}}{RCu + R^1C{\equiv}CEAlk_n}} \xrightarrow[H_2O]{THF} \underset{\text{(X)}}{\overset{H}{\underset{R^1}{>}}C{=}C\overset{R}{<}EAlk_n} + \underset{\text{(XI)}}{\overset{R}{\underset{R^1}{>}}C{=}C\overset{H}{<}EAlk_n};$$

Under these conditions, compounds with E = S form exclusively the isomer (XI), while compounds with E = N or O give rise preferentially to the isomer (X). Thus in the given instance the mode of addition of RCu to compound (IX) agrees with the changes in δC_{sp} as a result of the effect of E on the triple bond (Tables 3 and 9).

Electrophiles add to the triple bond in the compounds $RC{\equiv}CER^1$ (E = S, Se, Te) and in the analogous ethers in the same manner, but the mode of addition differs from that in hydrocarbons.[130,131] The addition of hydrogen chloride and bromide to alkylthio- and alkylseleno-vinylacetylenes always takes place at the triple bond and the halogen atom adds to the C_α atom:

$$CH_2{=}CH-C_\beta{\equiv}C_\alpha ER^1 \xrightarrow[X_2]{HX} CH_2{=}CH-CH{=}CXER^1;$$

E=S, Se; X=Cl, Br.

Comparison of the experimental data with the distribution of electron density in the molecules of 1-methylthio- and 1-methylseleno-but-3-en-1-ynes (without taking into account the *d* orbitals of the heteroatom) shows that the maximum electronic charge is concentrated on the β-carbon atom of the triple bond, which is consistent with the order and orientation of the electrophilic addition:[131,132]

$$\underset{-0.051}{CH_2}=\underset{-0.008}{CH}-\underset{-0.104}{C_\beta}\equiv\underset{0.014}{C_\alpha}-\underset{0.160}{S}-\underset{0.008}{Me}$$

$$\underset{-0.036}{CH_2}=\underset{-0.005}{CH}-\underset{-0.073}{C_\beta}\equiv\underset{0.003}{C_\alpha}-\underset{0.006}{Se}-\underset{0.006}{Me}$$

The ^{13}C NMR spectra of these compounds contain valuable information about the degree of conjugation of the heteroatoms (S, Se, Te) and the triple and double bonds.[22] The character of the polarisation of the triple bond (Table 8), indicating an enhancement of the electron-accepting properties on passing from alkylthio- to alkyltelluro-vinylacetylenes, conflicts with the data on the reactivities of these compounds.[22]

The data presented demonstrate yet again that the experimental values of δC_{sp} and the differences between them do not permit, despite the hypotheses expressed in the literature,[20,21] the prediction of not only the reactivity but also of the mode of addition of the reactants even in an isologous series of compounds. One of the causes of this is the "heavy atom effect" mentioned above, whose influence on the shielding of the C_{sp} atom in selenium-, bromine-, and especially tellurium-substituted acetylenic compounds cannot so far be estimated quantitatively.

The high reactivity of monosubstituted acetylenes in many reactions (acetylene condensation, Favorskii, Mannich, oxidative coupling, etc. reactions) is usually explained by the CH acidity, although little information is available about the equilibrium CH acidity. This is associated both with the difficulty of measuring the p*K* (which requires special apparatus and the use of dry media) and with the fact that certain derivatives (nitro-, alkoxycarbonyl, and other compounds) undergo side reactions under the conditions of the measurement (a highly basic medium). The acidity of monosubstituted acetylenes should be higher the lower the charge on the C_β atom. There are correlations between the energies of the heterolytic dissociation of the ≡C−H bonds and the charge on the ethynyl group[133] and also between the values of δC_β and the charge density on the same atom in *para*-substituted phenylacetylenes.[29] It therefore appeared useful to compare the values of δC_β with the p*K* for the monoacetylenic compounds. A linear relation has been observed between the p*K* for ethynylpyrazoles, the heterolytic dissociation energies of the ≡C−H bonds (the thermodynamic CH acidity of these compounds was measured in dimethyl sulphoxide by the transmetallation method[134,135]), and the charges on the ethynyl groups (calculated by the CNDO/2 method[133]).[136] These results agree with the fact that the relative rate of the Mannich reaction (piperidine, 35 °C) in the series of isomeric 3-, 4-, and 5-ethynyl-1-methyl pyrazoles is four times higher for the 5-C≡CH isomer than

for the 4-C≡CH isomer and 1.6 times higher than for the 3-C≡CH isomer.[137] However, a linear relation has not been observed between the pK or the charge $q\,C_\beta$ and the values of δC_β for these compounds. Presumably in the given series the shift δC_{sp} does not reflect the charge density.

The parallel variation of the acidities of *para*-substituted phenylacetylenes with δC_β and $\Delta\delta C_{\beta,\alpha}$ (Fig. 4) justifies the assumption that in the given series the shift $\delta C_{\beta(\alpha)}$ reflects the charge density on the atoms indicated.[29]

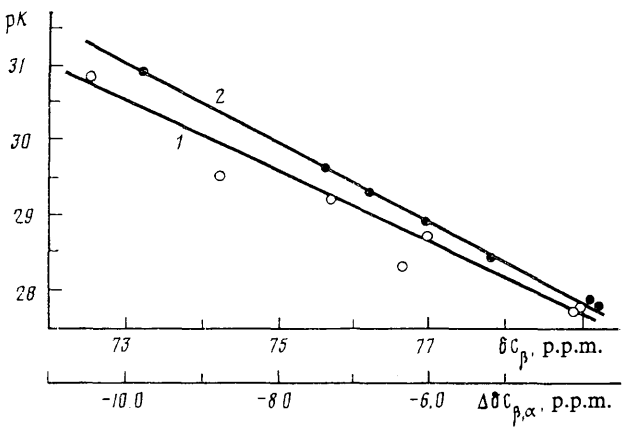


Figure 4. Dependence of pK on δC_β (line *1*) and $\Delta\delta C_{\beta,\alpha}$ (line *2*) in the series of ***para*-substituted phenylacetylenes (the values of δC_{sp} were taken from Klasine et al.[29]).**

A linear relation has also been observed reliably between the regiospecificity and stereospecificity of the nucleophilic addition of *p*-fluorophenol to *para*-substituted phenylacetylenes[138] and the values of δC_{sp}.[116]

On the whole, comparison of the calculated charge densities on the ethynyl carbon atoms[41,74] with the measured shifts δC_{sp} both for the simplest monosubstituted acetylenes[139] and for acetylenes containing heteroatomic substituents at the triple bond[140] does not exhibit a rigorous relation between these characteristics. This is associated primarily with the fact that substituents located close to the triple bond exert an appreciable steric and anisotropic influence on δC_{sp}.

Thus the relation between the reactivities of acetylenic compounds and the parameters of their ^{13}C NMR spectra is mainly qualitative. One of the main reasons for this is apparently the different distributions of electron density in the molecule, especially on the triple bond, in the stationary and dynamic states. Another possible explanation is the multifunctionality of the dependence of $\delta^{13}C$ on the structural parameters of the test compounds, which is not susceptible to a quantum-chemical description.

There is in general no justification for relating the degree of polarisation of the triple bond to the difference between the chemical shifts of the *sp*-carbon atoms or the overall charge on the triple bond to the sum of the shifts. This approach is valid only for chemical compounds in which the substituent is fairly reliably separated from the triple bond by a conformationally rigid fragment, for example, the benzene ring.

The state of the NMR theory at the present time is such that one can explain the available experimental facts rather than make predictions. There is no doubt about the usefulness of further studies on these lines, particularly if they are directed towards individual classes of reactions with participation of structurally similar acetylenic compounds.

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Periodicity of the change in properties in the series of *d*- and *f*-elements

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ABSTRACT. Many physicochemical properties in series of *d*- and *f*-elements change periodically with change in the number of *d*- or *f*-electrons in the d^q- or f^q-electron configurations. In the lanthanide and actinide series for a fixed electron configuration, the f^q-periodicity of the change in properties is called the tetrad or double–double relationship.

A number of properties of *d*-elements, lanthanides, and actinides depend on the initial d^q-, f^q- and final d^{q-1}-, f^{q-1}-electron configurations. These properties include the ionisation potentials of the free atoms and ions, electron affinity, redox potentials, excitation energies, and enthalpies of the decomposition and disproportionation of the halides, oxides, chalcogenides, and pnictides of the lanthanides and actinides, the oxidation state in compounds with variable oxidation states, etc. The present review analyses the regularity of the change in these properties in the lanthanide and actinide series, demonstrates the nature of the change in these properties, formulates a simple rule making it possible to predict unknown properties, and carried out an extensive comparison with the properties of *d*- and *p*-elements and their compounds. The properties of the trans-actinide *g*- and *h*-elements are predicted.

The bibliography contains 37 references.

Contents

I. Introduction 39
II. Systematics of the properties of the free atoms and ions 39
III. Experimental confirmation of the periodicity of the change in the properties of the free atoms and ions with change in the number of electrons 41
IV. Thermodynamic properties of compounds of the *f*-elements 43
V. Metals of the *d*- and *f*-series and intermetallic compounds 46

I. Introduction

With increase in the atomic number in the series of *f*-elements, the *f*-levels are gradually filled, leading to a similarity between the lanthanides and actinides. The similarity in many properties of their trivalent states is a long established fact. At the same time, the lanthanides and actinides exist in higher oxidation states: $Ln^{III,IV}$ and $An^{III-VII}$. In this way they show a similarity to the *d*-elements. Thus the actinides, showing a qualitatively new increase in the complexity of the electronic structure, resemble the lanthanides, but in their high and highest oxidation states they show a definite analogy with the *d*-elements. There is thus an overall regularity in the properties of the actinides, lanthanides, *d*-elements, and their compounds.

A number of recent papers have compared all these elements. Everyone who has studied, on the one hand, solid state physics, and on the other hand the chemistry of the simple and coordination compounds inevitably draws attention to the differences in the focus of the theoretical approaches in these branches of science. Qualitatively, however, both approaches lead to the conclusion that the light actinides are the analogues of the 3*d*-elements, rather than the 4*f*-elements. In each series, the behaviour of the electrons changes from delocalised bonding behaviour to localised non-bonding behaviour. At the same time, a group of elements show intermediate behaviour of the electrons: Ce, Pr, U, Np, Pu, Mn, and Fe. Subsequent analysis of experimental and theoretical data[1–3] has shown that there is a definite periodicity in the change in the physicochemical properties with change in the atomic number of the element in the *d*- and *f*-series. This periodicity covers a wide range of properties of both the free atoms and ions and their compounds, is general in character, and extends to the super-heavy compounds in the *g*- and *h*-series which have not yet been obtained.

II. Systematics of the properties of the free atoms and ions

Many physicochemical properties P of the lanthanides Ln and actinides An change periodically with change in the atomic number of the element or in the number of electrons q in a fixed f^q-electron configuration in accordance with the periodic change in the orbital quantum numbers L_q of the normal terms. Many examples of the existence of this periodicity can be given:[4] the change in the standard energy of extraction of the trivalent lanthanides, the ionic radii of the *d*- and *f*-elements in different charged states, the critical temperature of the appearance of superconductivity of the metals of the *d*-series, etc. In the final analysis, the periodic change in these properties is determined by the characteristic dependence of the quantum numbers L_q on q (Fig. 1) in the corresponding l^q-electron configurations (l = *d*-, *f*-, *g*-, and *h*-elements). Fig. 1 shows that in each series there is a characteristic double–double effect in the change in the properties P: d^0-d^5-d^{10}, f^0-f^7-f^{14}, g^0-g^9-g^{18}, h^0-h^{11}-h^{22}. Moreover, as a consequence of the two-fold symmetry with respect to the central pair in each half of the series d^2-d^3, d^7-d^8, f^3-f^4, f^{10}-f^{11}, g^5-g^6, g^{14}-g^{15}, h^7-h^8, h^{18}-h^{19} for the quantum numbers L there are respectively pairs of triads, tetrads, pentads, and hexads in the *d*-, *f*-, *g*-, and *h*-series.

Thus in the series of *s*-, *p*-, *d*-, *f*-, *g*-, and *h*-elements it is possible to construct definite sequences of electron configurations depending on the number of electrons and the quantum numbers L_q: s^0-s^1, s^1-s^2; p^0-p^1, p^2-p^3; d^0-d^2, d^3-d^5; f^0-f^3, f^3-f^7; g^0-g^4, g^5-g^9; h^0-h^5,

h^6-h^{11}. Similar sequences can be constructed in the second halves of the series, with a displacement by a number of electrons equal to the number of electrons in the half-filled levels.

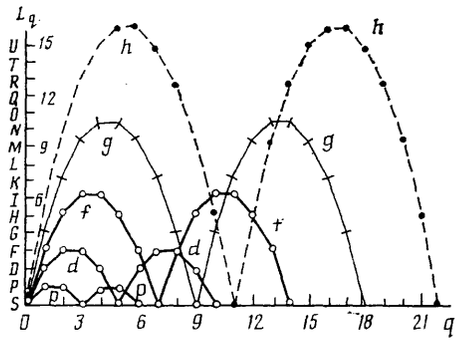


Figure 1. Plot of the quantum numbers L_q against the number of electrons q in the series of *s*-, *p*-, *d*-, *f*-, *g*-, and *h*-elements.[12]

1. Redox processes

If the electron configurations of the atoms or ions change in a reaction, the periodicity of the change in properties depends on the quantum numbers L_q and L_{q-1} in the initial and final electron configurations f^q and f^{q-1} or d^q and d^{q-1}. The ionisation equilibrium $f^q \rightleftharpoons f^{q-1} + e$ and $d^q \rightleftharpoons d^{q-1} + e$ ($L_q \rightleftharpoons L_{q-1}$), corresponding to a redox reaction, can be examined. It will be assumed that there exists a temperature range in which there are only two kinds of ion containing q and $q-1$ electrons; for example doubly- and triply-ionised, or triply- and quadruply-ionised ions, etc. The condition for chemical equilibrium can then be written as

$$E_0/kT = \ln(\zeta_q n_q/\zeta_{q-1} n_{q-1}), \quad (1)$$

where E_0 is the absolute magnitude of the difference in the energies of the non-split normal terms of the l^q- and l^{q-1}-electron configurations, n_q and n_{q-1} the numbers of ions in these configurations, and ξ_q and ξ_{q-1} the values of the corresponding distribution functions or the multiplicities of the degeneracy of the normal terms with respect to the quantum numbers M_L for fixed spin quantum numbers S. The parameter α giving the probability that an ion has the oxidised electron configuration d^{q-1} or f^{q-1} can be introduced. In the high-temperature limit $kT \gg E_0$,

$$\alpha = \frac{n_{q-1}}{n_q + n_{q-1}} = \left[\left(1 + \frac{\zeta_q}{\zeta_{q-1}}\right)\exp(-E_0/kT)\right]^{-1} = \frac{2L_{q-1}+1}{2L_q + 2L_{q-1} + 2}, \quad (2)$$

which corresponds to ionisation equilibrium. The dependence of α on q for *p*-, *d*-, *f*-, *g*-, and *h*-elements is shown in Fig. 2*a*, which demonstrates the periodicity in the change in the redox properties in each half of the series with increase in the atomic number or the number of electrons q. This periodicity is revealed in the sharp–retarded–sharp change in properties in each half of the series. The sharpest change in properties is observed on going from the first to the second half of the series. For the elements of the *f*-series, with allowance for the equalities

$$L_q = q(7-q)/2, \; q \leqslant 7; \; L_q = (14-q)(q-7)/2, \; q > 7 \quad (3)$$

it is possible to rewrite Eqn. (2) as follows

$$\alpha = \frac{9q - q^2 - 7}{16q - 2q^2 - 6}, \; q \leqslant 7; \; \alpha = \frac{23q - q^2 - 119}{44q - 2q^2 - 216}, \; q > 7. \quad (4)$$

This dependence of α on q covers a wide range of properties: ionisation potentials, electron affinity, redox potentials, excitation energies, etc. The section of the plateau corresponding to the retarded change in properties is not observed for the *p*-elements; for two-electron reactions $d^q - d^{q-2} + 2e$ the section of the plateau becomes indistinct, and the dependence of α on q is close to linear.

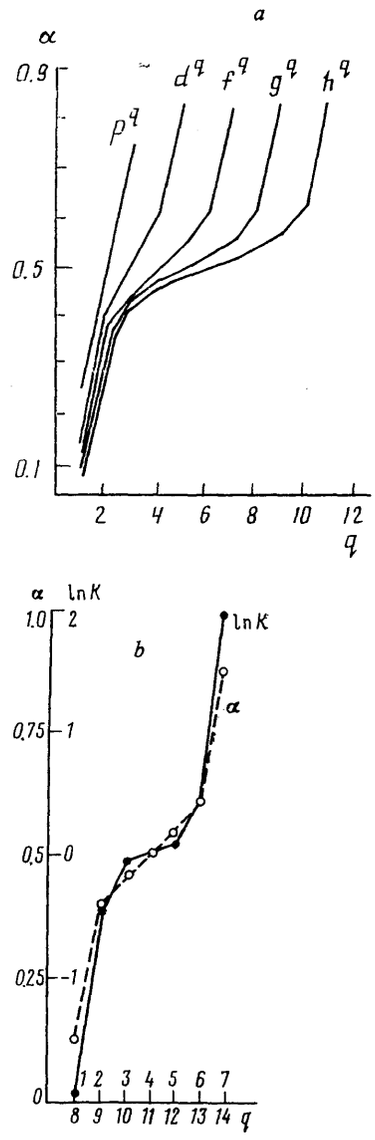


Figure 2. Dependence of the parameter α on the number of electrons for various elements[4] (*a*) and the dependence of the parameters α and $\ln K$ on the number of electrons (*b*) in the series of *f*-elements.

Similar conclusions are reached for the constants K of the ionisation equilibrium $f^q \overset{K}{\rightleftharpoons} f^{q-1} + e$ for a monatomic gas consisting of f-ions. The free energy for this reaction, $F = -RT \ln K$, depends on the number of electrons q and $q-1$, the quantum numbers L_q and L_{q-1}, and the ionisation energy I_q (Fig. 2*b*). At $T \simeq I_q$ the periodicity of $\ln K$ with change in q is determined by the difference $\Delta L = L_{q-1} - L_q$

$$\ln K \approx 2\,(L_{q-1} - L_q)\,(L_{q-1} + L_q + 1)^{-1}. \qquad (5)$$

The section of the plateau corresponding to elements for whose oxidised and reduced forms the values of ΔL are low, are shown in Fig. 2*b*.

2. The rule of intervals in redox processes

In the LS-coupling approximation, the d-, f-, g-, and h-levels have internal symmetry, according to which, for the normal terms of the ions with the electron configurations l^q, where $l \equiv d, f, g, h$, the quantum numbers L_q and S_q are given by the equations

$$\text{for } q<7\text{: } L_q = q(2l+1-q)/2,\ S_q = q/2;$$
$$\text{for } q>7\text{: } L_q = (4l+2-q)(q-2l-1)/2,\ S_q = (4l+2-q)/2. \qquad (6)$$

Eqns. (2) and (6) lead to the simple rule of intervals in the change in the properties P_q with change in q in the d- and f-series of elements.

For the f-elements:

$$\text{for } q \leqslant 7,\ c=0\text{: } (P_{1+c}+P_{7+c}):P_{4+c} = (P_{2+c}+P_{6+c}):P_{4+c} = (P_{3+c}+P_{5+c}):P_{4+c} = 2;$$
$$\text{for } q>7,\ c=7\text{: } (P_{1+c}+P_{7+c}):(P_{2+c}+P_{6+c}) = (P_{2+c}+P_{6+c}):(P_{3+c}+P_{5+c}) = 1;$$

For the d-elements:

$$\text{for } q \leqslant 5,\ e=0\text{: } (P_{1+e}+P_{5+e}):P_{3+e} = (P_{2+e}+P_{4+e}):P_{3+e} = 2;$$
$$\text{for } q>5,\ e=5\text{: } (P_{1+e}+P_{5+e}):(P_{2+e}+P_{4+e}) = 1.$$

It is important to emphasise that these expressions relate the properties of different elements of the same series. For example, in the first half of a series, the ratio $(P_{1+c} + P_{7+c}):P_{4+c}$ is determined by the properties of the ions with the electron configurations $f^1(^2F)$, $f^7(^8S)$, and $f^4(^5I)$: the triply-charged ions of thorium, curium, and neptunium, or the quadruply-charged ions of protactinium, berkelium, plutonium, etc. These relationships are particularly useful for those elements whose properties are difficult to measure because they are available in only small quantities or are highly radioactive, etc.

For redox reactions in each half of a series, inversion of the normal term takes place relative to the element for which it does not change:

$$d^1 \to d^0 + e\text{: } D \to S;\quad d^5 \to d^4 + e\text{: } S \to D;$$
$$d^2 \to d^1 + e\text{: } F \to D;\quad d^4 \to d^3 + e\text{: } D \to F;$$
$$d^3 \to d^2 + e\text{: } F \to F.$$

For the elements of the d-, f-, g-, and h-series, these reactions are:

$$d^3 \to d^2 + e;\quad f^4 \to f^3;\quad g^5 \to g^4;\quad h^6 \to h^5$$
$$F \to F \qquad I \to I \qquad N \to N \qquad U \to U\ .$$

III. Experimental confirmation of the periodicity of the change in the properties of the free atoms and ions with change in the number of electrons

1. Excitation energies

For neutral atoms, the periodic character of the change in the excitation energies with change in the number of electrons $f^{q-1}ds^2 \to f^q ds$, $f^q ps$, $f^q s^2$, $f^q d^2$ has been noted in a number of studies.[2,4,9] The presence of the electrons in the dsp-atomic orbitals and the similarity in the energies of several electron configurations for the elements of the start of the actinide series, however, lead to slight departures from the predictions of periodicity theory. For lanthanide and actinide atoms in f^q-electron configurations, when the one-configuration approximation is sufficiently correct, the dependence of the excitation energies on q is close to the theoretical. This leads to the rule of intervals for the excitation energies (Table 1). For a comparison of the p-, d-, and f-elements, Fig. 3 gives various excitation energies calculated from spectral data.[5–8] They confirm the periodicity in the change in excitation energies, the existence of the plateau section for the d- and f-elements, and its absence for the p-elements. In addition, the experimental values of the excitation energies E for the doubly-charged ions of the $3d$-series,[5] $3d^q \to 3d^{q-1}4s$, satisfy the relationships

$$[E\,(\text{Ti}) + E\,(\text{Gr})]/E\,(\text{V}) = 1.99;\quad [E\,(\text{Fe}) + E\,(\text{Zn})]/E\,(\text{Ni}) = 2.00;$$
$$[E\,(\text{Co}) + E\,(\text{Cu})]/E\,(\text{Ni}) = 1.99,$$

confirming the applicability of the rule of intervals for these ions.

The excitation energies of the free atoms and ions correlate with many properties of their compounds:[10–13] redox potentials, energy of cohesion of the metals, and thermodynamic stability; these properties determine the semiconducting, superconducting, and magnetic properties, etc. In the chemistry of the lanthanides and actinides, the solution of the problem of the localisation or delocalisation of electrons is related primarily to the question of the excitation of the electrons and their transfer to an unoccupied d-level. This range of problems makes it important to study the regularities of the change in the excitation energies with change in the atomic number of the elements.

2. Ionisation potentials

Jørgensen[11] expressed the ionisation energy of f-electrons in terms of the parameter V defining the reference point, the energy of stabilisation of the f-electrons from one element to another $E - A$, the spin–orbit splitting energy ζ, and the parameter D, defined as a linear combination of Slater–Condon integrals:†

$$q=1\text{: } I_1 = V + 2\zeta;\quad q=2\text{: } I_2 = V + (E-A) + (^8/_{13})D + 9E^3 + \zeta;$$
$$q=3\text{: } I_3 = V + 2(E-A) + (^{16}/_{13})D + 12E^3 + {}^1/_2\zeta;$$
$$q=4\text{: } I_4 = V + 3(E-A) + (^{24}/_{13})D;$$
$$q=5\text{: } I_5 = V + 4(E-A) + (^{32}/_{13})D - 12E^3 - {}^1/_2\zeta;$$
$$q=6\text{: } I_6 = V + 5(E-A) + (^{40}/_{13})D - 9E^3 - \zeta;$$
$$q=7\text{: } I_7 = V + 6(E-A) + (^{48}/_{13})D - 2E^3 - 2\zeta;$$
$$q=8\text{: } I_8 = V + 7(E-A) + (^{48}/_{13})D + {}^3/_2\zeta,$$
$$q=9\text{: } I_9 = V + 8(E-A) + (^{40}/_{13})D + 9E^3;$$
$$q=10\text{: } I_{10} = V + 9(E-A) + (^{32}/_{13})D + 12E^3 + {}^1/_2\zeta;$$
$$q=11\text{: } I_{11} = V + 10(E-A) + (^{24}/_{13})D;$$
$$q=12\text{: } I_{12} = V + 11(E-A) + (^{16}/_{13})D + 21E^3 - {}^1/_2\zeta.$$

† Jørgensen[11] gives estimates of the parameters used for the Ln^{3+} ions: $E - A \simeq 3000$ cm^{-1}, $D \simeq 6500$ cm^{-1}; the values of ξ change from 650 cm^{-1} to 2950 cm^{-1} on going from Ce^{3+} to Yb^{3+}. In the examination of the relative change in the ionisation potentials in the f-series, the values of the one-electron energies V are excluded.

Table 1. Change in the excitation energies[7,8] illustrating the rule of intervals.[1,2,13]

No.*	$(f^x+f^y):f^{(x+y/2)}$	An^{2+}			An^{3+}			Ln^{3+}			Ln^{3+}		
		6d	7s	7p	6d	7s	7p	5d	6s	6p	5d	6s	6p
1	$(f^1+f^7):f^4$			1.88	2.03	1.92	1.96	1.98	1.92	1 93	1.98	1.97	1.96
2	$(f^2+f^6):f^4$			1.96	1.95	1.97	1.98	1.93	1.98	1.98	1.99	1.99	1 99
3	$(f^3+f^5):f^4$			1.98	1.98	1.99	2.00	1.98	2.00	2.00	2.00	2.00	2.00
4	$(f^8+f^{14}):f^{11}$	1.90	1.84	1.95	1.95	1.96	1.97	1.84	1.97	1 90	1.97	1.99	1.97
5	$(f^9+f^{13}):f^{11}$	1.95	1.92	1.98	1.98	1.98	1.99	1.89	1.98	1.97	1.98	1.99	1.99
6	$(f^{10}+f^{12}):f^{11}$	1.99	1.98	2.01	1.99	1.99	2.00	1.98	1.99	1.98	1.99	1.99	2.00
7	$(f^1+f^7):(f^2+f^6)$			1.04	1.00	0.97	1.01	1.01	1.02	0.98	1.00	0.99	1.00
8	$(f^2+f^6):(f^3+f^5)$			1.02	0.98	1.01	1.01	1.02	1.02	1.04	1.01	1.00	1.00
9	$(f^8+f^{14}):(f^9+f^{13})$	0.97	1.04	1.01	0.99	0.99	0.95	0.97	0.99	0.96	1.01	0.99	1.00
10	$(f^9+f^{13}):(f^{10}+f^{12})$	1.00	1.03	0.98	1.01	1.01	1.00	1.02	1.00	1.01	1.01	1.00	1.00

* The theoretical values are 2.00 for ratios 1–6, and 1.0 for ratios 7–10.

From these expressions it follows that

$(I_1 + I_7) : I_4 = (I_2 + I_6) : I_4 = (I_3 + I_5) : I_4 = (I_8 + I_{14}) : I_{11} = (I_9 + I_{13}) : I_{11} = (I_{10} + I_{12}) : I_{11} = 2.00$.

Table 2 gives the corresponding relationships for the doubly- and triply-charged lanthanides and actinides.

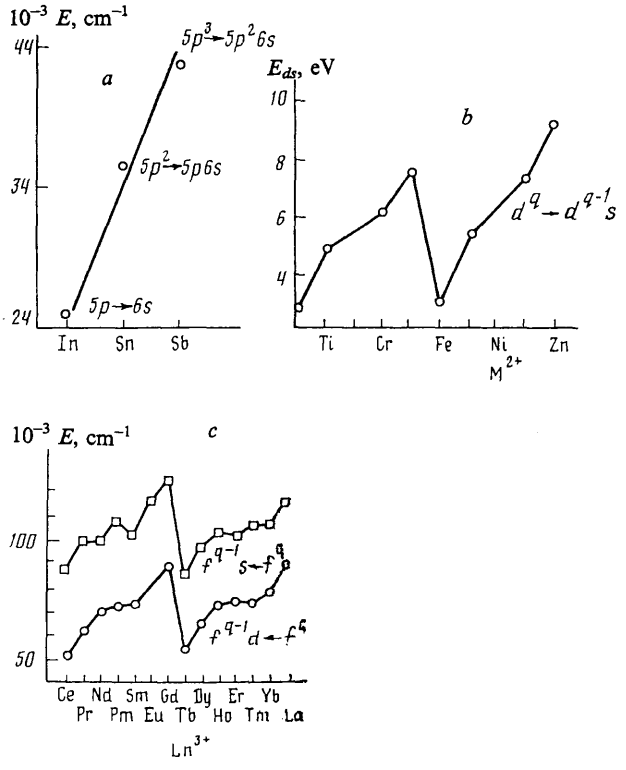


Figure 3. Excitation energies for elements of the *p*- (*a*), *d*- (*b*), and *f*-series (*c*): $p^q \rightarrow p^{q-1}s$; $d^q \rightarrow d^{q-1}s$; $f^q \rightarrow f^{q-1}s$.

3. Redox potentials

Fig. 4 illustrates the periodicity of the change in the oxidation potentials for $E^0(An^{2+}/An^{3+})$, $E^0(Ln^{3+}/Ln^{4+})$, and $E^0(An^{4+}/An^{5+})$, which have been measured or calculated. The general trends in the change in the potentials $E^0(An^{+}/An^{2+})$, $E^0(An^{2+}/An^{3+})$... for the actinides are shown in Fig. 5, from which it can be seen that the numbers of the atoms corresponding to the so-called plateau section are displaced with change in the oxidation state. For example, for the actinides:

E^0(II/III) — Pa, U, Np;
E^0(III/IV) — U, Np, Pu;
E^0(IV/V) — Np, Pu, Am.

This displacement is characteristic of the ranges corresponding to the sharp and sharpest changes in the properties in both series, lanthanides and actinides.

Table 2. Change in the ionisation potentials of the lanthanides[12] and actinides[13] illustrating the rule of intervals.[1,2,13]

Ratio of the ionisation potentials	Ln^{2+}	Ln^{3+}	Ln^{4+}	An^{2+}	An^{3+}
$(f^1+f^7):f^4$	1.99	1.97	1.98	2.065	1 95
$(f^2+f^6):f^4$	1.97	1.99	1.99	2.09	2.00
$(f^3+f^5):f^4$	1.98	2.02	1.99	2.035	2.00
$(f^8+f^{14}):f^{11}$	2.00	1.99	1.99	2.00	1.99
$(f^9+f^{13}):f^{11}$	1.99	1.99	1.99	2.045	1.99
$(f^{10}+f^{12}):f^{11}$	1.99	1.99	1.99	1.99	1.99
$(f^1+f^7):(f^2+f^6)$	1.01	1.02	1.00	0.99	0.97
$(f^2+f^6):(f^3+f^5)$	0.99	1.00	1.01	0.97	1.00
$(f^8+f^{14}):(f^9+f^{13})$	0.99	0.99	0.99	0.99	0.99
$(f^9+f^{13}):(f^{10}+f^{12})$	1.00	1.00	1.00	1.00	1.00

IV. Thermodynamic properties of compounds of the *f*-elements

1. Hydrated ions

The chemistry of aqueous solutions, and allowance for the influence of hydration on the physical and chemical properties of ions, represent an extensive and varied problem. Water is a strongly polar solvent, in which both cations and anions are solvated, and in which even the hydrated electron may be formed. The effects of lanthanide and actinide ion hydration have been studied by a number of authors.[15–17] In particular, the solubility, conductivity, relative viscosity, free energies of hydration, and equilibrium constants of aqueous solutions of lanthanide salts, etc. have been measured.

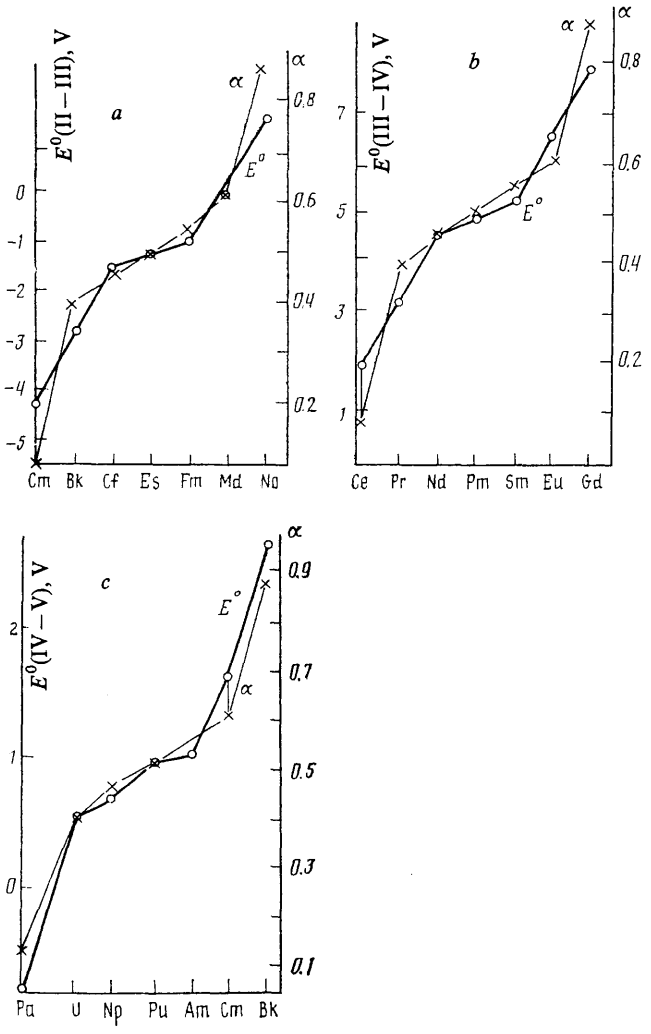


Figure 4. Periodicity of the change in the redox potentials in the lanthanide and actinide series.

The behaviour of lanthanide and actinide ions in solution is characterised by a number of specific features. Thus in aqueous solutions the dependence of the thermodynamic and transport properties on the number of electrons is regular for the light ions from La to Nd and the heavy ions from Tb to Lu, whereas the properties change in the opposite sense for the ions from Pm to Gd. This unusual behaviour for the *f*-series is due to the nature of the interaction of the *f*-ions with water molecules and the change in the coordination number of the lanthanides with change in the number of electrons of the ion. Similar studies were later carried out for actinide ions.[16] The electronic structures of the hydrated ions have been calculated.[18] All these experimental and theoretical studies show that the chemical bonds in the hydrated ions are partly covalent, as revealed by a variety of physicochemical properties. The important role of the second coordination sphere in hydration in different solutions has been revealed. Although the problem of the aqueous solutions of the lanthanides and actinides is complex and varied, a number of general semi-empirical and empirical relationships in the structures of the hydrated ions and the thermodynamic properties are firmly established (Fig. 6).

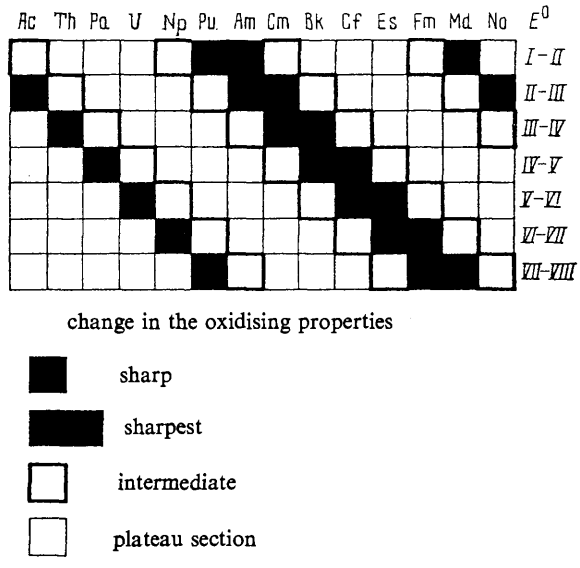


Figure 5. Diagram of the change in the oxidising properties of the actinides.

With increase in the number of electrons q in the f^q-electron configurations, the partial molar volumes $\overline{V}^0_m$ decrease for the light lanthanides (f^0–f^4), increase for the elements of the middle of the series (f^5–f^8), and decrease again for the heavy lanthanides (f^9–f^{14}) (Fig. 6*a*); that is, there are three clearly defined regions of change in $\overline{V}^0_m$.

The total number of water molecules h surrounding the ion, and the number of water molecules n_m in the first hydration shell, change in the opposite sense with increase in the number of electrons q for both series (Ln and An). The curves giving the dependence of h and

n_m on q show two plateaux for the light and heavy elements. A crossed analogy is observed for the lanthanides and actinides: a short plateau section for the light lanthanides and heavy actinides, and a long plateau section for the heavy lanthanides and the light actinides (Figs. 6*b* and 6*c*).

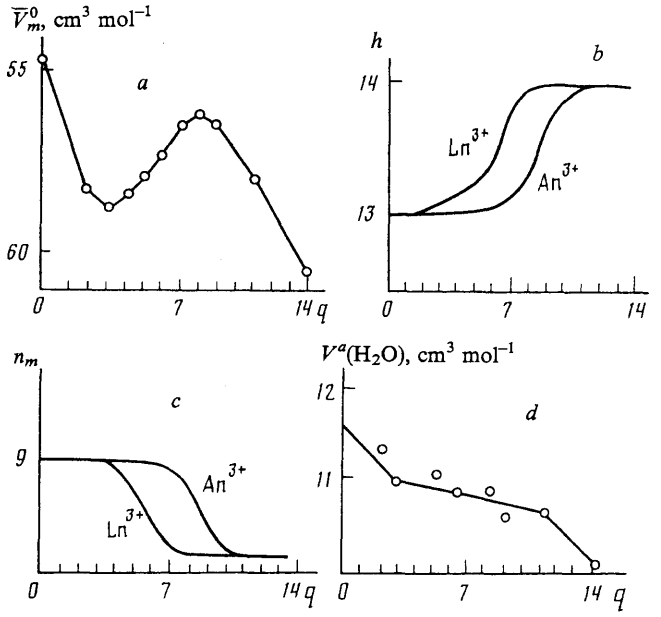


Figure 6. The three types of dependence of the properties of the triply-charged lanthanide and actinide ions in solution on the number of electrons: *a*, partial molar volumes; *b*, number of water molecules in the first and second hydrate layers; *c*, number of water molecules in the first hydrate layer; *d*, average volume of a bound water molecule in the hydrate layer.

The sections of intermediate change in h and n_m in the lanthanides and actinides are displaced: for the lanthanides this section lies in the first half of the series (Pr, Sm, Eu, and Gd), and for the actinides it lies in the second half (Cm, Bk, Cf) (Figs. 6*b* and 6*c*).

The average volume of the water molecules in the hydration shell (Fig. 6*d*) decreases with increase in the number of electrons q; a sharp decrease in volume is observed at the beginning and end of the series, and a plateau in the middle.

The thermodynamic properties of the aquo-ions have been analysed.[19] The enthalpy of hydration H_h for Ln^{3+} and An^{3+} changes regularly and almost linearly along the series, except for the elements in the middle of the series. The components of H_h, however, that is the enthalpy of formation of the aquo-ions $H(Ln^{3+}_{aq})$ and the cations $H[Ln^{3+}(gas)]$ change irregularly and in opposite directions, due to the existence of the compensation effect. As a result, the dependence of H_h on q for Ln^{3+} and An^{3+} is close to linear. This makes it possible to calculate the quantity $H_h(An^{3+})$ using approximate equations, for example:[20]

$$H_h = \frac{7.32Z^2(An^{3+})}{R+0.85},$$

where R is the radius of the ion with charge Z, and the constant 0.85 characterises the change in the radius of the ion in solution.

2. Halogen compounds of divalent and trivalent lanthanides and actinides

Since the halogen compounds of the lanthanides and actinides have important practical applications, their properties, in particular their thermodynamic properties, have been studied by many authors, by both experimental[21–24] and theoretical[25,26] methods. The enthalpies of formation of $LnHal_3$ have been determined by mass spectrometry, solution calorimetry, etc., and also calculated from the equation

$$H_0[MX(crystalline)] = H_0[M^{Z+}(gas)] + \frac{A}{R_{M^{Z+}} + R_X} + B,$$

$$H_0[M^{Z+}(gas)] = H_{sub}(M) + \sum_{i=1}^{3} I_i + {}^5/_2 ZRT,$$

where $R_{M^{Z+}}$ is the ionic radius of the metal, R_X the radius of the anion, A and B are constants, $H_{sub}(M)$ the standard enthalpy of sublimation, and $\sum_{i=1}^{3} I_i$ the sum of the ionisation energies; the last term represents the change in enthalpy as a function of temperature for an ideal gas.

According to published data,[25,26] the enthalpy of formation of $LnHal_3$ shows an irregular dependence on the number of f-electrons. In addition to the features of the structure of the f-levels characteristic of Ln^{3+}, revealed by the change in the values of H_{sub} and $\sum_{i=1}^{3} I_i$, the irregular change in $H_0(LnHal_3)$ with change in the number of f-electrons is also related to a change in the type of crystal structure. Thus in the trifluorides, the tetragonal LaF_3 structure is replaced in the second half of the series by the hexagonal–trigonal α-YF_3 structure. At the same time there is a change in the coordination number of the metal: with increase in the number of electrons q for the $Ln^{3+}(f^q)$ ion, the ninth fluorine atom is, as it were, displaced from the first coordination sphere, so that, for example, for HoF_3 and YbF_3 the internuclear distance Ln–F for one of the nine fluorine atoms is greater by 0.20 Å and 0.34 Å respectively[27] than the average Ln–F distance for the other eight fluorine atoms. This effect is similar to that observed for the aquo-ions, where the number of water molecules in the first coordination sphere changes from nine to eight on going from the ions of the light elements to the ions of the heavy elements.

At all stages of the development of the theory of the compounds of the trivalent f-elements, new examples of chemical regularities have been discovered. These regularities show a common feature, however, namely a regular change in properties for the light and heavy elements, and an anomalous change for the intermediate elements. The section of the anomalous relationship may include a larger or smaller number of elements, depending on the type of ligand, but for these elements there is always a change in the coordination number, internuclear distances, structure, etc.

The existence of three regions of change in the crystal-chemical properties is reflected in the melting points T_f and the enthalpies of solution. Thus the compounds LnF_3 can be divided into three groups, depending on the values of T_f: the heavy Dy–Lu, the light La–Nd, and the intermediate Nd–Dy.[28]

The difference between the lattice enthalpy of a crystalline compound H_c and the enthalpy of hydration of the ionic components determines the enthalpy of solution H_s. For $LnHal_3$,[21] the change in structure, for example for $EuF_3 \rightarrow GdF_3$ or $GdCl_3 \rightarrow TbCl_3$, is due to the anomalous change in H_s.

The experimental values of H_c are known for the chlorides of the actinides of the middle of the series:[21] for UF_3, H_c = −1502 kJ mol^{-1}, and for PuF_3, H_c = −1586 kJ mol^{-1}; for the chlorides of uranium, plutonium, americium, and curium, the corresponding values are −866, −960, −978, and −974 kJ mol^{-1}; for the bromides of uranium, neptunium, and plutonium, H_c = −699, −730, and −793 kJ mol^{-1}; and for the iodides of these metals, H_c = −467, −513, and −580 kJ mol^{-1} respectively. Solution calorimetry has been used to measure the standard enthalpies of formation of $CsSmCl_3$, $CsTmCl_3$, and $CsYbCl_3$.[29] The last two compounds have the ideal perovskite structure, and $CsSmCl_3$ and $CsEuCl_3$ have a distorted perovskite structure. The experimental values of H_0 for the synthesised compounds $CsLnCl_3$ and the calculated values for $CsNdCl_3$ and $CsDyCl_3$ correlate with the corresponding values for $LnCl_3$:

Ln in $CsLnCl_3$	Nd	Sm	Dy	Tm	Yb
H_0, kJ mol^{-1}	−1124	−1230	−1165	−1194	−1285

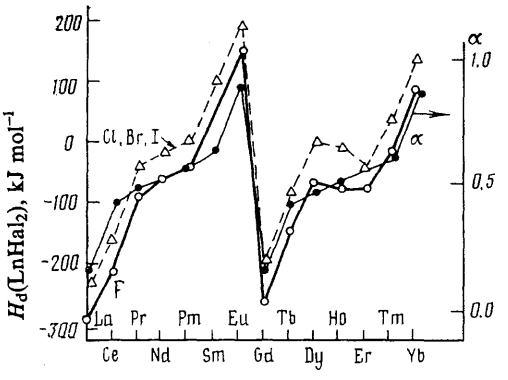


Figure 7. Dependence of the parameter α and the free enthalpies of decomposition (H_d) according to the scheme $LnHal_2 \rightarrow {}^1/_3Ln + {}^2/_3LnHal_3$ on the atomic number of the element.

The standard enthalpies of formation of the corresponding compounds $LnHal_2$ and $LnHal_3$, and also $AnHal_2$ and $AnHal_3$, can be used to calculate the standard enthalpies of the disproportionation

$$MHal_2 \rightarrow {}^1/_3M + {}^2/_3MHal_3$$

where M = Ln or An. The principal quantity determining the nature of the change in the enthalpies of decomposition with change in atomic number is not the sum of the ionisation potentials, as in the case of the enthalpies of formation, but the difference in the sums of the ionisation potentials, that is the third ionisation potential. This leads to a periodic change in the values of the enthalpies of decomposition in accordance with the periodic change in the ionisation potentials and the parameter α. This leads to the characteristic dependence of the enthalpies of decomposition on the number of electrons (Figs. 7 and 8).

3. Halogen compounds of tetravalent lanthanides and actinides

Experimental studies of the thermodynamic characteristics of the tetrafluorides are limited to the mass-spectral analysis of TbF_4 and CeF_4, tensimetric measurements for CeF_4, PrF_4, and TbF_4, and calorimetric measurements for CeF_4 and TbF_4 in an HCl + H_3BO_3 mixture.[24] The experimental values of $H_0(LnF_4)$ show a large scatter.

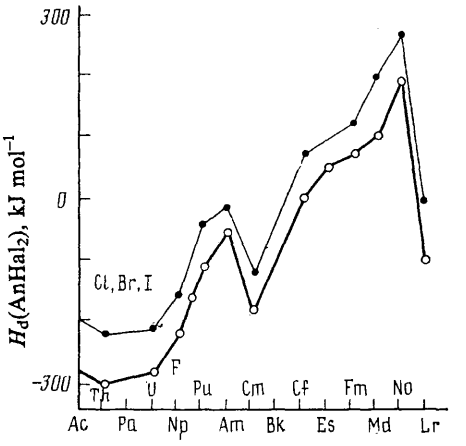


Figure 8. Dependence of the standard enthalpies of decomposition (H_d) according to the scheme $AnHal_2 \rightarrow {}^1/_3An + {}^2/_3AnHal_3$ on the atomic number of the element.

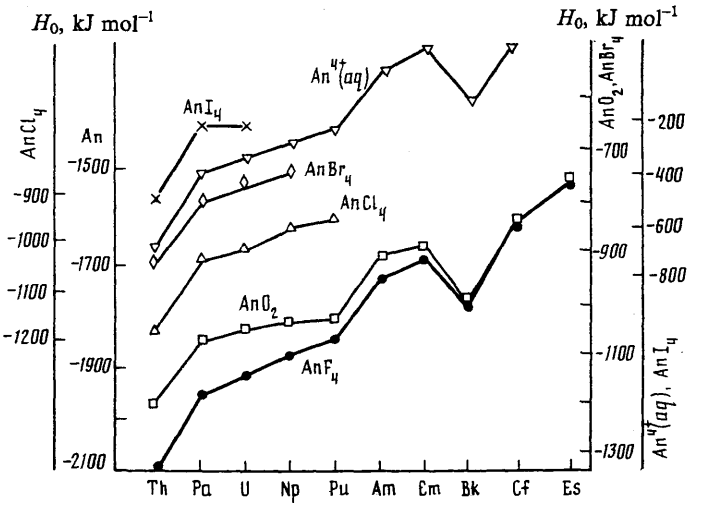


Figure 9. Dependence of the standard enthalpies of formation on the atomic number of the element.

The thermodynamic properties of the actinide tetrahalides ThF_4, PaF_4, UF_4, NpF_4, PuF_4, and AmF_4 have been studied experimentally.[21] Even for thorium tetrafluoride, however, the standard enthalpies of formation measured in fourteen studies show a scatter in the values of about 36 kJ mol^{-1}. Fig. 9 gives the dependence of the measured and calculated enthalpies of formation of the actinide tetrahalides in solution on the number of *f*-electrons. The data for

AnO_2 and $An^{4+}(aq)$ [21] are given for comparison. A noteworthy feature is the clearly defined plateau for Pa(f^1), U(f^2), Np(f^3), and Pu(f^4) and the sharp change in the enthalpies of formation on going from Th(f^0) to Pa(f^1) and from Pu(f^4) to Am(f^5) in the first half of the series. The same characteristics are observed for the compounds of the lanthanides.

The values of the enthalpy of decomposition of the tetrahalides

$$MHal_4 \rightarrow Hal + MHal_3$$

are determined by the difference

$$\sum_{i=1}^{4} I_i - \sum_{i=1}^{3} I_i.$$

Thus the rule of intervals formulated above is also applicable in this case.

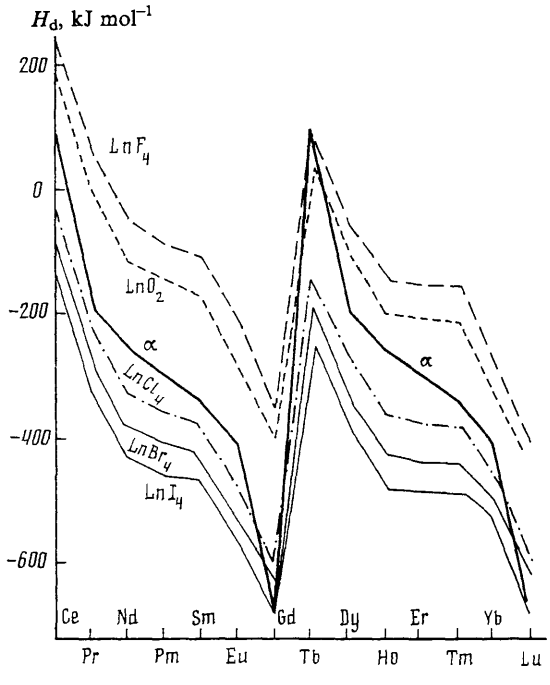


Figure 10. Dependence of the standard enthalpies of decomposition according to the scheme $LnX_4 \rightarrow X + LnX_3$ on the atomic number of Ln.

4. Oxides and chalcogenides

Of the lanthanide monoxides, EuO and impurity YbO have been characterised; in the monoxides LaO, CeO, PrO, NdO, and SmO, two valence electrons from the lanthanide atom are used for chemical bond formation, and the third for the formation of the conductivity band. Monoxides of Th, U, Np, Pu, and Am, formed on the surface of the metals, are known. The monoxide PuO is also obtained by reducing the dioxide PuO_2 using Pu and C; AmO is formed by the reaction of Am with HgO or in the gas phase. The standard enthalpies of formation of LnO and AnO have been calculated.[25,26]

For various lanthanides existing in the divalent state, for example La, Ce, Gd, and Lu, the one-configuration approximation is inadequate, and it is necessary to take account of several electron configurations involving *d*- or *s*-orbitals: $f^q + f^{q-1}d + f^{q-1}s \ldots$ In this case the rule of intervals for the disproportionation $MO \rightarrow {}^1/_3M + {}^2/_3MO_{1.5}$ should not apply. If however the electron configuration of the lanthanide f^q in the divalent state is stable, the rule of intervals applies.

In Fig. 10 the standard enthalpies of the decomposition $LnO_2 \rightarrow {}^1/_2O + LnO_{1.5}$ are compared with the corresponding values for $LnHal_4$. The characteristic periodicity of the change in these values with change in the number of electrons is again observed. Irrespective of the ligands, for all compounds of the tetravalent lanthanides and actinides, the standard enthalpies of decomposition change in accordance with the theoretical dependence of α on *q*. This periodicity should also be observed for higher oxidation states, for example for An_2O_5 (An = Pa, U, Np, Pu, ...), where the series includes hypothetical compounds.

For the sulphides and pnictides of the lanthanides and actinides, according to calculations of the standard enthalpies of formation of MS, $MS_{1.5}$, MS_2, and MAs, where M = Ln or An,[25,26] the same trends are observed in the change in these quantities with increase in the atomic number as in the case of the corresponding oxides, that is for the systems MO and MS, $MO_{1.5}$ and $MS_{1.5}$, and MO_2 and MS_2. An analogy is also observed in the dependence of the standard enthalpies of decomposition to the metal and the corresponding sulphide on the number of electrons.

V. Metals of the *d*- and *f*-series and intermetallic compounds

1. Crystal structures and electron configurations

Fundamental studies of the metallic lanthanides and actinides have been carried out in recent years, and the results reviewed.[30–35] In these studies, the role of the 4*f*- and 5*f*-electrons in the formation of the metallic bond was extensively discussed. Many problems have been resolved, but there is still no answer to the main question, namely the actual electron configurations of the atoms in the metals and the oxidation states of various actinides in the metals.

In accordance with the main purpose of the present review, which is to follow the regularity in the change in various properties of the lanthanides, actinides, and their compounds and to compare them with other series of elements, this task will also be carried out for the *d*- and *f*-metals.

In the lanthanide series, all the metals are trivalent, except Eu and Yb, and in the actinide series the heavy elements are divalent in the metallic state, the light actinides include tetravalent metals, and the intermediate elements are trivalent. In the actinide series, anomalous effects associated with a change in oxidation state will be superimposed on the periodicity in the change in properties due to the structure of the 5*f*-level.

The light metallic actinides (as far as plutonium) have crystal structures with a low symmetry; for plutonium, six different phases exist in the temperature range from 298 K to 913 K. Distorted and complex structures are generally formed if the 5*f*-electrons are involved in the production of the metallic band. The crystal structures of the heavy metals resemble the structures of the metallic lanthanides. The crystal structures are different for the light and

heavy actinides. The largest number of phases is observed for the metals in the middle of the series.

The crystal structure depends on the energy of excitation from the electron configurations of the ground state into low-lying excited states. Thus in the lanthanide series, where the 4*f*-electrons remain practically non-bonding, the crystal structure is determined by the valence *d*- and *s*-electrons, that is by the electron configurations: $f^q ds^2$, $f^q d^2 s$, $f^q dsp$, $f^{q+1} s^2$, $f^{q+1} ds$, $f^{q+1} sp$. If the neutral atom has the electron configuration $f^q ds^2$, then in the metal with the double hexagonal structure its electron configuration changes from $f^q d^{1.3} sp^{0.7}$ to $f^q d^{0.9} sp^{1.1}$.[33] If in the free state the atom has the electron configuration $f^{q+1} s^2$, then in the metal with the double hexagonal structure it changes from $f^{q+1} d^{0.3} sp^{0.7}$ to $f^{q+1} sp$.

2. Melting points of the metallic actinides

The change in the melting point T_f in the series of metallic actinides reflects their complex electronic structure. On going from metallic thorium to einsteinium, T_f changes from 2023 K to 1133 K. Even for metals having delocalised 5*f*-electrons, such as Pa, U, Np, and Pu, the melting point changes from 1840 K to 913 K. The dependence of T_f on the atomic number of the element is shown in Fig. 11. At high temperatures close to the corresponding melting points, the heavy metals (from Am to Es) have a face-centred cubic structure, and the light actinides (from Th to Np) a body-centred cubic structure.

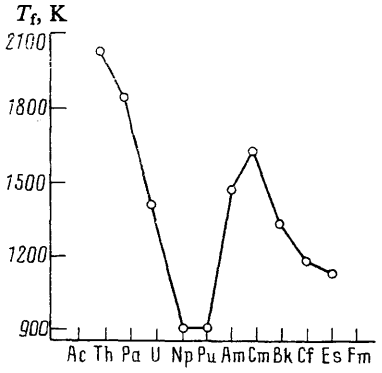


Figure 11. Dependence of the melting points of the metallic actinides on the atomic number.

The melting point T_f of the metal depends on the atomic number of the element. It decreases on going from Th to Np and Pu, increases from Pu to Am, and then decreases regularly from Cm to Fm. There is a correlation between the T_f values and the orbital quantum numbers L_q of the normal terms of the actinide ions: Th(f^0), Np(f^3), Pu(f^4), Am (f^6), Cm(f^7), Bk(f^8) (Fig. 12). These electron configurations correspond to the tetravalent states for the light actinides (from Th to Pu), the trivalent states for the elements of the middle of the series (from Bk to Am), and to divalent states for the heavy actinides (from Es to No).

The populations of the valence orbitals in the metals are fractional. The values for the 5*f*-orbitals are apparently greater than those indicated above. Fig. 12 shows clearly that the electron configurations Th(f^0), Np(f^3), Pu(f^4), Am(f^6), Cm(f^7), and Bk(f^8) have a significant influence on the production of the electronic structure of the atoms in the metals.

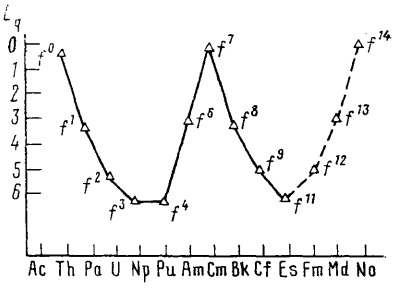


Figure 12. Change in the orbital quantum numbers L_q of the normal terms of the actinide ions with change in q.

3. Bond lengths in the metals and atomic volumes

The bond lengths in metals are fundamental characteristics and determine many of their properties—atomic volumes, band width, bond strength, etc. Data on the dependence of the atomic radii on the atomic number of the element have been compared for the metals of the *d*-series and the actinides.[31] For the metals of the 3*d*-series, the dependence is close to parabolic, and shows a double–double effect similar to that observed for the ionic radii in various compounds of these elements. This effect is revealed more clearly for the metals of the 3*d*-series than for the metals of the 4*d*- and 5*d*-series, since the 3*d*-electrons are more localised.

The almost parabolic dependence of the metallic radii on the atomic number is responsible for the same behaviour of the atomic volumes of the metals of the *d*-series.

The lanthanides Eu and Yb show anomalous values of the atomic volumes. This is related to the fact that Eu and Yb are divalent. From the corresponding relationship for the atomic volumes of the metallic actinides it was concluded[35] that the light actinides (from Th to Pu) are tetravalent.

4. Energies of cohesion

a) Metals of the *d*-series

The change in the energy of cohesion E_c for the metals of the 3*d*-series[35] is described by a curve which is close to parabolic, with a minimum at the middle of the series. The parabolic relationship breaks down for metallic manganese, although significant anomalies are not observed for the manganese analogues technetium and rhenium.

Among the metals of the 3*d*-series, Ca, Ni, and Cu have a face-centred cubic structure, Sc, Ti, and Co a double hexagonal structure, and V, Cr, and Fe a body-centred cubic structure; metallic manganese has a complex crystal structure with several non-equivalent atoms in the cell. The metals of the 4*d*-series have different crystal structures: Sr, Rh, Pd, Ag have a face-centred cubic structure; Ru and Cd a double hexagonal structure; and Nb and Mo a body-centred cubic structure. In these crystals, the metal atoms have the electron configurations $d^{q-x} sp^x$ and $d^q s$; the

contribution of the *p*-orbitals is greater for the double hexagonal system than for the face-centred or body-centred cubic structures.

Spectroscopic data[5] can be used to estimate the sum of the energies of excitation from the electron configurations $3d^q4s^2$ of the ground state of the neutral atoms Sc, Ti, V, Mn, Fe, Co, and Ni into the electron configurations $3d^{q+1}4s$ and $3d^{q+1}4s4p$. Since in the ground state the Cr and Cu atoms have the electron configurations d^5s and $d^{10}s$ respectively, for these elements it is possible to take account of only the excitation into the electron configurations d^5p and $d^{10}p$. For the calcium atom, account was taken of the sum of the excitation energies $4s^2 \rightarrow 4s4p + 4s3d$, and for the zinc atom only the energy of the single excitation $4s^2 \rightarrow 4s4p$ was considered.

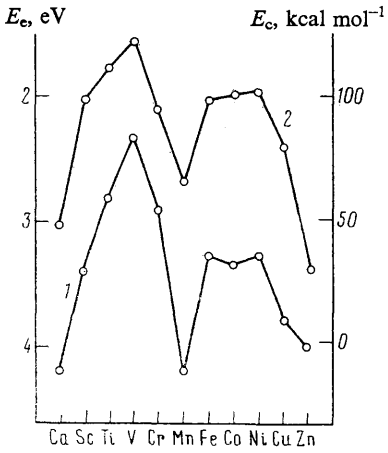


Figure 13. Correlation between the energy of cohesion of the metals and the sum of the energies of excitation from the electron configuration of the ground state d^qs^2 (Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Zn) and d^qs (Cr, Cu) into the electron configurations d^qsp and d^qs; for each excited electron configuration, the multiplet of lowest energy is used.

It is obvious that the greater the excitation energy (E_e) corresponding to the electron configuration of a given type of crystal lattice, the lower the energy of cohesion, that is an inverse relationship exists between these quantities. The sum of the excitation energies reflects completely the energies of cohesion of the metals of the 3*d*-series (Fig. 13). The existence of the plateau section on the graph giving the dependence of E_c on the atomic number for metallic Fe, Co, and Ni (Fig. 13) is due to the opposed trends in the change in the excitation energies of the free atoms. The values of the energies of excitation from the electron configurations of the ground state d^qs^2: Fe(d^6s^2, ^5D), Co(d^7s^2, ^4F), and Ni(d^8s^2, ^3F), into the electron configurations $d^{q+1}s$ and d^qsp can be considered. These values (in eV), together with the electron configurations and their terms, are given below:

	$3d^{q+1}4s$	$3d^q4s4p$
Fe (d^6s^2; ^5D):	2.4 ($^5F_5$);	0.86 ($^7D_5$)
Co (d^7s^2, ^4F):	2,93 ($^4F_{9/2}$);	0.43 ($^6F_{11/2}$)
Ni (d^8s^2, ^3F):	3.44 ($^3D_4$);	0.03 ($^5D_4$) .

The sums of these quantities differ little, leading to similar values of the excitation energy for the atoms and approximately equal energies of cohesion for these metals. Thus the properties of the free atoms correlate well with the properties of the metals; this applies both to the energies of cohesion and the moduli of compression of the metals (Fig. 14). Thus the relationship between the corresponding energies of excitation and energies of cohesion or moduli of compression is apparently close to linear.

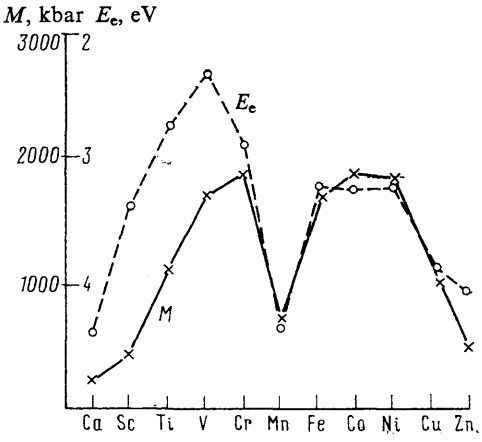


Figure 14. Correlation between the modulus of compression (M) for the metals of the 3*d*-series and the energies of excitation (E_c) into the hybrid state.

b) Metallic actinides

The dependence of E_c for the metallic actinides on the excitation energies has been studied.[33–36] Account was taken of the excitation energies[7,8] $f^qs^2 \rightarrow f^{q-1}ds^2$ and $f^{q-1}ds^2 \rightarrow f^{q-2}d^2s^2$ on going from the divalent to the trivalent and then to the tetravalent state. From this approach it was concluded[36] that Am, Cm, and Bk are trivalent. The valence of Cf is intermediate between 2 and 3, and the heavy metallic actinides, beginning with einsteinium, are divalent. For metallic Np and Pu, the picture is more complex and indefinite. From estimates of the excitation energies $f^{q-1}ds^2 \rightarrow f^{q-2}d^2s^2$ it follows that Np and Pu in the metallic state are apparently trivalent, but estimates of the atomic volumes and other properties indicate that they are tetravalent.

If for the light actinides (from thorium to plutonium) account is taken of the energies of excitation into the formally tetravalent states, accompanied by unpairing of the $7s^2$ electron pair, $f^{q-2}d^3s$ and $f^{q-2}d^2sp$, then the nature of the change in the excitation energy for Np, Pu, and Am will not reflect even the trend in the change in E_c. If however it is assumed that the hybrid functions in the metallic state are complex and are formed from several electron configurations: $f^{q-1}d^2s + f^{q-1}dsp + f^{q-2}d^3s + f^{q-2}d^2sp$, and that the contribution of the last two electron configurations is small, then it is possible to obtain not only a qualitatively correct description but also a quantitative description of the dependence of E_c on the excitation energy. In the second half of the series, the values of the energy of cohesion correlate with the energies of

excitation into both the divalent and the trivalent states. If it is assumed that Bk and Cf are trivalent in the metallic state, and that all the actinides from einsteinium onwards are divalent, the energies of cohesion of the metallic forms of these elements again do not agree with the experimental data. For the berkelium atom, the energies of excitation into the formal divalent and trivalent states are approximately equal. Thus the metallic state apparently corresponds to several electron configurations: f^8d^2s, f^8dsp, f^9sp.

Thus for the heavy metallic actinides, the change from Cm^{III} to No^{II} takes place in stages. To conclude this section, it may be noted that in the interpretation of the properties of the actinides it is incorrect to take account of only one electron configuration for each valence state: f^qs^2 for An^{II}, $f^{q-1}ds^2$ for An^{III}, and $f^{q-2}d^2s^2$ for An^{IV}, with integral values of the populations of the *f*-, *d*-, and *s*-orbitals. On going from Th to Pu there is an increase in the energies of excitation into the electron configurations $f^{q-2}d^3s$, $f^{q-2}d^2sp$, and $f^{q-2}d^2s^2$, indicating a decrease in their contribution to the overall electron configuration in the metals. Similarly, in the second half of the series, there is a gradual decrease in the contribution of the electron configurations $f^{q-1}d^2s$ and $f^{q-1}ds^2$ to the electron configurations of the metals, and the contributions from the f^qsp- and f^qsd-electron configurations increase.

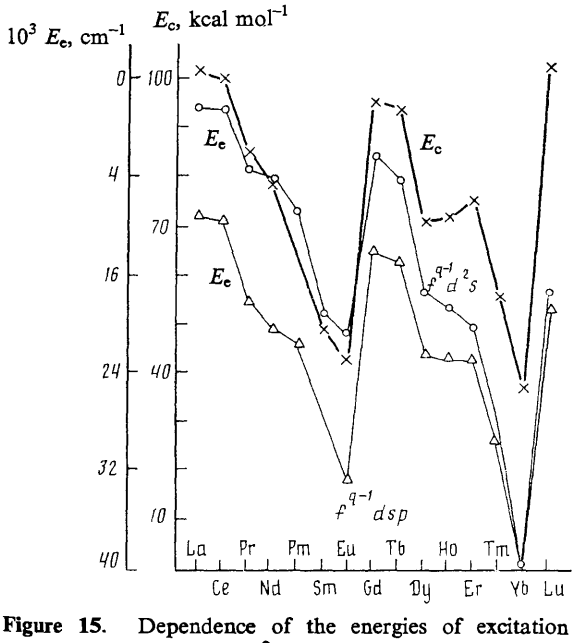


Figure 15. Dependence of the energies of excitation from the electron configuration f^qs^2 into the electron configurations $f^{q-1}d^2s$ and $f^{q-1}dsp$ on the atomic number of the element; in the first case the configurations $f^7ds + f^7d^2$ for Eu and $f^{14}ds + f^{14}d^2$ for Yb were used, and in the second case $f^7p^2 + f^7sp$, $f^7dp + f^7ds$ for Eu and $f^{14}ds + f^{14}dp$ for Yb; it can be seen that there is a correlation between the energies of excitation and cohesion E_c.

c) Metallic lanthanides

The dependence of the energy of cohesion of the metallic lanthanides on the atomic number reflects the periodicity in the properties of the free atoms more clearly than any other property. Fig. 15 gives the dependence of the energies of excitation from the electron configuration of the ground state f^qs^2 into the electron configurations $f^{q-1}d^2s$ and $f^{q-1}dsp$ for all the elements except Eu and Yb, for which the energies of excitation into the divalent states were used.[4] The changes in the energies of cohesion and in the energies of excitation with change in the atomic number show a remarkable similarity.

Comparison of the energies of cohesion for the metals of the *d*-series, the lanthanides, and the actinides shows that the atomic factor is preserved to the greatest extent for the metals of the 3*d*-series and the lanthanides, in accordance with the fact that the 4*f*-electrons are more localised than the 5*f*-electrons, and the 3*d*-electrons more localised than the 4*d*- and 5*d*-electrons.

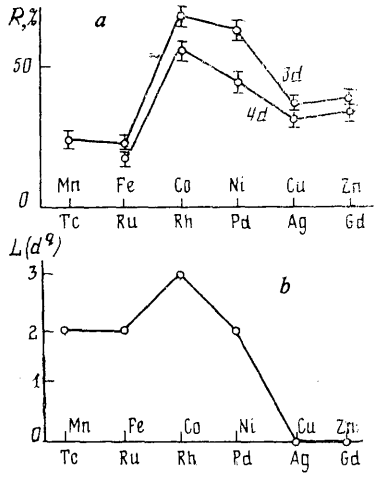


Figure 16. Ranges of change in composition (R) for the intermetallic compounds with metals M (*a*) and the dependence of the quantum numbers L for the electron configurations of the atoms M (*b*) in the metals ($d^qs^xp^y$) on the atomic number of M.

5. Intermetallic compounds of the lanthanides

The lanthanides form a large number of compounds with different compositions with the metals of the *s*-, *p*-, and *d*-series, and the regularities in the change in their properties can be followed. The most widely encountered compounds of the lanthanides with metals are the following: Ln_3M, Ln_5M_2, Ln_7M_5, Ln_9M_4, $Ln_{24}M_{11}$, Ln_2M, Ln_2M_{17}, Ln_5M_3, Ln_3M_2, Ln_4M_3, Ln_5M_4, $Ln_{11}M_{10}$, LnM, Ln_5M_{41}, Ln_6M_7, Ln_3M_4, Ln_7M_{10}, Ln_3M_5, LnM_2, LnM_3, Ln_2M_7, $Ln_{14}M_{51}$, Ln_3M_{11}, Ln_5M_{19}, Ln_6M_{23}, Ln_3M_{22}, LnM_4, Ln_4M_{17}, Ln_5M_{22}, $Ln_{13}M_{58}$, Ln_5M_{24}, LnM_5, LnM_6, LnM_7, LnM_{11}, LnM_{13}, LnM_{66}, etc. The relative concentration of Ln in the two-component compounds is restricted. The highest concentration of Ln in these compounds is apparently achieved in Ln_3M. The composition of the simplest compounds changes regularly for each system. These compounds are LnM_2 for the elements Mn, Tc, Re, and Fe, Ln_3M for the other transition elements, LnM for the elements of groups IB and IIB (except Au), and Ln_3M again for the elements of groups IIIA, IVA, and VA. A definite periodicity in the composition is observed. The most varied compositions with respect to M are shown by the compounds of the lanthanides with the group IIB

elements, whereas the elements from Al to Bi are characterised chiefly by the compounds LnM_3. Boron gives a large number of compounds with different compositions.

The composition of the compounds is determined chiefly by the electronic structure of M, that is by the number of *d*-, *s*-, and *p*-electrons for M. All the lanthanide compounds can be divided into three groups, depending on the electronic structure of M: 1) compounds with transition elements, 2) compounds with IB and IIB elements (except Au), and 3) all other compounds. If the range of change in the composition (R) of the compounds with respect to M is defined as the difference $R = R_u - R_l$, where R_u and R_l are the upper and lower percentage concentrations of M in the compounds with the highest and lowest concentrations of M, then an extremal value of R is reached in the middle of the second half of the series of *d*-elements (Fig. 16). This reveals a characteristic of the *d*-levels occupied to the extents of 1/2, 3/4, and 1, that is the values of R should correlate qualitatively with the values of the quantum numbers L_q for the normal term and the d^q-electron configurations corresponding to the hybridisation of the atoms in the pure metals: Mn, Tc (d^6s); Fe, Ru ($d^{6-x}p$); Co, Rh ($d^{8-x}sp^x$); Ni, Pd (d^9s); Cu, Ag ($d^{10-x}sp^x$); Zn, Cd ($d^{10}sp$).

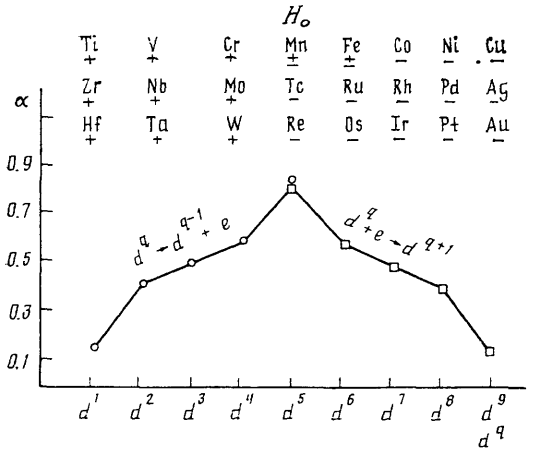


Figure 17. Dependence of α on q, showing that the most stable compounds of the 3*d*-metals with the lanthanides should be formed by the heavy 3*d*-metals; the upper part of the Figure gives the signs of the heats of formation of the compounds LnM.

The curve describing the dependence of the percentage concentration of the compounds LnM relative to the total number of compounds on the percentage concentration of M in the given type of compound is bell-shaped (the apex of the bell corresponds to the compounds LnM_2, the largest class of compound). The number of compounds with a given composition increases in the order: $Ln_5M_3 < LnM_3 < LnM < LnM_2$. In the reaction of the metals of the 5*d*-series and the lanthanides, the greatest bonding is achieved with the *d*-elements of the second half of the series. In their reaction with the elements of the first half of the 3*d*-series, the lanthanides should be reduced, and in their reaction with the elements of the second half they should be oxidised. Correspondingly, the 3*d*-elements in the first half of the series are oxidised, and those in the second half are reduced. The dependence on q of the values of $\alpha = [2L_{q+1} + 1][2L_{q+1} + 2L_q + 2]^{-1}$ for the first half of the series and $\alpha = [2L_{q-1} + 1][2L_{q-1} + 2L_q + 2]^{-1}$ for the second half determines the tendency to undergo oxidation on going from the d^5- to the d^1-electron configuration and to undergo reduction on going from the d^5- to the d^9-configuration. These trends are shown schematically in Fig. 17, which also gives the signs of the heats of formation of the intermetallic compounds H_0. The electron configuration d^5s^2 was used for all the *d*-elements.

The heavy *d*-elements act as electron acceptors $Ln^{\delta+}M^{\delta-}$, and the acceptor properties increase towards the end of the series (Fig. 17). The light *d*-elements should be electron donors, $Ln^{\delta-}M^{\delta+}$, and the donor properties should increase from the middle to the beginning of the series. Thus since they have a low electron affinity, the lanthanides should not tend to form intermetallic two-compounds with the light *d*-elements. The sign of the heat of formation is not always known for the middle of the series.

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The present review has analysed the general regularities in the change in the redox properties of the lanthanides, actinides, and elements of the *d*-series. This phenomenon is determined by the specific features of the electrostatic interaction of the *d*- or *f*-electrons. It leads to a characteristic change in the properties with increase in the number of electrons: a sharp–retarded–sharp change in each half of the series, and the sharpest change on going from one half of the series to the other.

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Specific features of the chemical structure of the oxo-complexes of d^0 and d^2 metals with monodentate and polydentate ligands

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ABSTRACT. The structure of the oxo-complexes of transition d^0 and d^2 Group V–VII metals is discussed. Two types of distortion isomerism are considered: the *trans*-influence isomerism (the lengthening of the M=O multiple bond on passing from one isomer to another is accompanied by a shortening of the M–L_{trans} bond) and the multiple bond isomerism (the lengthening of the M=O bond is not accompanied by a shortening of the M–L_{trans} bond). The choice of the *trans*-partner out of the set of competing functional groups for the d^0 metal is determined by the self-consistency principle, while for the d^2 metal the rule becomes more complex and the choice of the *trans*-partner of the oxo-ligand depends on the individual features of the *trans*-ligand (on the combination of its σ- and π-donor properties). It is shown in relation to the d^0-MoO_2 and d^2-ReO complexes with isotypical chelate O, N-donor ligands that the latter are coordinated to the metal in different ways.

The bibliography includes 58 references.

Contents

I. Introduction 52
II. The lability of the length of the M=O multiple bond in complexes of d_1 and d_2 metals 53
III. The choice of the *trans*-partner in complexes of d^0 and d^2 metals 54
IV. The *trans*-influence isomerism in mixed halogeno-phosphine complexes of d^2 metals 56
V. Analysis of the disposition of the chelate organic ligands in oxo-complexes of d^0 and d^2 metals 58

I. Introduction

The stereochemistry of transition metal complexes with ligands linked by multiple bonds and in particular the stereochemistry of d^0 and d^2 metals has now been investigated comprehensively by Soviet and foreign workers. It is distinguished by the following principal features.

1. The mutual disposition of the ligands X linked by multiple bonds in octahedral dioxo-complexes of Group V–VII is determined by the electronic configuration of the metal: *cis*- and *trans*-dispositions occur for the d^0 and d^2 metals respectively.[1–3] This rule has a completely evident model quantum-chemical interpretation. The *cis*-disposition of two or (three) ligands linked by multiple bonds in complexes of d^0 metal ensures the maximum involvement of all three t_{2g} orbitals of the octahedral metal polyhedron (or, in other words, the d_{xy}, x_{xz}, and d_{yz} orbitals) in the π-acceptance of electrons by the multiple bond-linked ligands X. The *trans*-disposition of two multiple bond-linked ligands in complexes of the d^2 metal is determined by the fact that this ensures the minimum electron-electron repulsion between the orbital occupied by the lone electron pair of the metal and the π- and σ-electrons of the bond formed by the ligands X (Fig. 1)†.

2. The *trans*-influence of the X≡M...L multiple bond, manifested by the lengthening (weakening) of the bond with the *trans*-partner, depends on the nature and multiplicity of the bond involving the ligand X, the nature of the *trans*-partner L, and the electronic configuration of the metal M:[4] (a) the *trans*-influence diminishes in the following series of ligands X:

$$M\equiv > N\equiv > O\equiv > RN\equiv > =O\equiv > ON\rightleftarrows, OC\rightleftarrows;$$

(b) the bond with a neutral donor ligand L (the *trans*-partner of the multiple bond-linked ligand X) is weakened to a greater extent than the bond with the acido-ligand L^{n-}; (c) depending on the electronic configuration of the metal, the *trans*-influence diminishes in the sequence $d^0 \geqslant d^1 > xd^2$.[5]

3. The choice of the *trans*-partner from the set of competing functional groups is determined by the self-consistency principle.

It has been shown[6] that the *trans*-influence of the multiple bond-linked ligand is transmitted via the σ-mechanism: the π-interaction, leading to the shortening of the X–M distance, increases σ-overlap and hence the σ-exchange integral between X and M, diminishing it in the region of M and L_{trans}. The most "convenient" *trans*-partners are therefore as a rule *N*- and *O*-donors (in particular ammonia and water molecules), the degree of localisation of the lone pairs of which can vary within wide limits in such a way that the equilibrium X–M–L_{trans} configuration is obtained for the given multiple bond-linked ligand X.

Thus the labilising effect exerted by the multiple bond-linked ligand on the bond between the metal and the *trans*-partner makes preferable the participation of the least polarisable σ-donor in this bond. As will be shown below, the application of this rule to d^2 metals is complicated by other factors.

The structural manifestation of the *trans*-influence of the multiple bond—the lengthening of the bond with the *trans*-partner—can be conveniently characterised quantitatively by the parameter Δ, which is defined as the differences between the lengths of the bonds formed by the metal with the *trans*-partner and with the analogous ligand located in the *cis*-position relative to the multiple bond. In the absence of like ligands simultaneously in the *cis*- and

† The complexes of d^1 metals with multiple bond-linked ligands X usually have a dinuclear structure with a *cis*-disposition of the terminal and bridging ligands X, which is also characteristic of d^0 metals.

trans-positions, it is necessary to use the parameter Δ', defined as the difference between the length of the bond with the *trans*-partner and the standard (ST) mean statistical length of the bond with an atom of the same kind in the usual complexes (not containing multiple bond-linked ligands). In order to estimate such standard Mo–O, Mo–N, and Mo–S distances, we employed the structural data presented in a monograph‡.[5] On their basis, one can postulate the following typical ranges of bond lengths: $Mo-O_{trans}$ = 2.11–2.38 Å, $Mo-O_{ST}$ = 1.94–2.08 Å (Δ_{av}' = 0.25 Å), $Mo-N_{trans}$ = 2.26–2.45 Å, $Mo-N_{ST}$ = 2.11–2.26 Å (Δ_{av}' = 0.20 Å); $Mo-S_{trans}$ = 2.63–2.80 Å, $Mo-S_{ST}$ = 2.42–2.51 Å (Δ_{av}' = 0.25 Å).

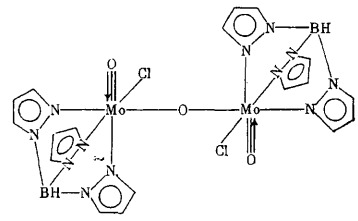
As already mentioned, the *trans*-influence diminishes in the sequence d^0 metals > d^1 metals > d^2 metals. We shall quote two examples. In the series of oxo-halogenometal complexes having the general formula $K_2[M^VOX_5]$, where M = d^0-Nb and X = F,[7] M = d^1-Mo and X = Cl,[8] and M = d^2-Re and X = Cl,[9] the quantity Δ diminishes correspondingly from 0.23 to 0.21 and 0.08 Å on passing from d^0 to d^1 and d^2 metals. Admittedly in the given instance, not only the electronic configuration but also the nature of the metal varies, so that this example is not entirely convincing. The comparison of compounds of heptavalent and pentavalent rhenium, namely $Re^{VII}O_3(ReO_4)(H_2O)_2$ [10] and $Re^VOI_2(ReO_4)(PPh_3)_2$, is much clearer.[11] At first sight, the difference between the lengths of the bonds with the *trans*-partner of the oxo-ligand—the oxygen atom of the perrhenate anion—is not very great: the decrease in the $Re-O_{trans}$ distance on passing from d^0-Re(VII) to d^2-Re(V) is only 0.07 Å (2.10 and 2.03 Å respectively). However, one should bear in mind that in the case of Re(VII) we are dealing with the trioxo-complex ReO_3^+, where the Re=O bonds are purely double bonds, while in the case of Re(V) we are dealing with a monoxo-complex ReO^{3+} formally containing a triple bond (Re≡O), which affects the Re–O (oxo) bond length (1.76 and 1.67 respectively). The increase in the multiplicity of the bond in the second compound enhances the *trans*-influence; therefore in the case of a pure Re=O double bond in the Re(V) complex, the $Re=O_{trans}$ distance should be significantly smaller than 2.03 Å.

II. The lability of the length of the M=O multiple bond in complexes of d^1 and d^2 metals

The vast majority of data concerning the structures of octahedral complexes with multiple bond-linked ligands refers to oxo-compounds. The the complexes of d^0 metals, the length of the metal–oxygen multiple bond is fairly stable and depends on the number of oxo-oxygen atoms in the complex (on the multiplicity of the bond). Thus, in the most numerous Mo(VI) compounds, the length of the formally triple Mo≡O bond (monoxo-complexes) is 1.61–1.68 Å, while the length of the bond having formally a multiplicity of 2.5 (dioxo-complexes) is 1.67–1.72 Å. In some of the trioxo-complexes investigated, the MoO=O double bonds have a length of approximately 1.74 Å.

‡Strictly speaking, in an estimate of this kind one should take into account in addition data obtained in recent years and a definite classification of O-, N-, and S-containing ligands (neutral-donor and acido-ligands, monodentate and polydentate ligands, ligands without multiple bonds in metallocycles and with multiple bonds, etc.) should be made.

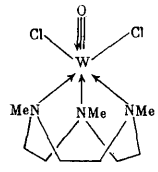
In the complexes of d^1 and especially d^2 metals, the length of the multiple bond is less constant regardless of the number of oxo-oxygen atoms. This is clearly seen from the data presented in Table 1. Depending on the nature of the outer-sphere cation and the number of molecules of water of crystallisation, the Mo–O distance in the three $[Mo^{IV}O(CN)_4(H_2O)]^{2-}$ complexes varies within the limits of 0.12 Å.[12,13] The Mo=O distances differ even more in two conformational isomers of the dinuclear complex $[Mo^VOCl\{HB(Pz)_3\}]_2(\mu\text{-}O)$ with a bridging oxygen atom.[14] The isomers differ in the local symmetry of the complexes: in the C_i isomer (I)



(I): isomer C_i

the bridging oxygen atom is located at the centre of inversion, while in the other isomer (C_2) it is located on the two-fold symmetry axis passing at right angles to the N–Mo–O–Mo–N axial coordinate. In the C_i isomer, the $Mo=O_{end}$ bond is longer by 0.109 Å than in the C_2 isomer.

The two crystalline modifications of the paramagnetic complex $[WOCl_2L](PF_6)$ (II), presented in Table 1, have different colours and are not geometrical isomers, but are almost identical as regards the conformation of the tridentate ligand L.[15]



(II)

These two forms differ mainly only by the length of the bond between the tungsten and oxygen atoms and the bond between the tungsten atom and the nitrogen atom (of the ligand L) in the *trans*-position. In the blue form, the first distance is smaller by 0.17 Å and the second distance is greater by 0.05 Å than in the green form (Δ = 0.13 and 0.17 Å respectively).

It is remarkable that these two forms persist also in solution: in anhydrous acetone they do not undergo a change in the colour characteristic of their solid state. One is therefore dealing not with crystalline modifications but with a special type of isomerism.

Table 1 shows that the range of variation of the M≡O bond lengths in the Mo complexes examined reaches 0.18 Å and, when account is taken of the compound of tungsten whose atomic radius differs little from that of molybdenum, the range increases to 0.29 Å. In all the compounds compared, a decrease in the stretching vibration frequency ν(M=O), accompanied by a change in the colour of the crystals from blue to green, corresponds to the increase in the length of the M=O bond.

Table 1. Geometrical parameters and vibration frequencies $\nu(M=O)$ of the complexes of d^2 and d^1 metals with a labile M=O double bond.

Formula	Colour of complex	Electronic configuration	Bond lengths, Å			Δ(Δ′)	$\Delta_{M=O}$*, Å	$\nu_{M=O}$, cm^{-1}	Refs.
			M=O	M−L_{trans}	M−L_{cis}				
$Kat_2[MoO(CN)_4(H_2O)]\cdot nH_2O$									
Kat=$AsPh_4$, n=4	Blue	d^2	1.60	2.48 (H_2O)	2.19 (CN)	(+0.39)	0.12	980	[12]
Kat_2=Pt(En)$_2$, n=2	Blue		1.668	2.271 (H_2O)	2.16 (CN)	(+0.18)	0.052	970	[13]
Kat=PPh_4, n=4	Green		1.72	2.96 (H_2O)	2.13 (CN)	(+0.87)	—	920	[12]
$(PPh_4)_3[MoO(CN)_5]\cdot 7H_2O$	Green	d^2	1.705	2.373 (CN)	2.168 (CN)	+0.205	—	920	[12]
$[WOCl_2L](PF_6)$ **	Blue	d^1	1.72	2.37 (NR_3)	2.24 (NR_3)	+0.13	0.17	980	[15]
	Green		1.89	2.32 (NR_3)	2.25 (NR_3)	+0.07	—	960	[15]
$[MoOCl\{HB(Pz)_3\}]_2(\mu\text{-}O)$	Brown (C_2)	d^1	1.670	2.313 (NR_2)	2.169 (NR_2)	+0.144	0.109	966	[14]
	Brown (C_i)		1.779	2.277 (NR_2)	2.179 (NR_2)	+0.098	—	960	[14]

*$\Delta_{M=O}$ is the difference between the M=O bond lengths in two isomers (green−blue or C_2-C_i).
**L = *N*, *N*′, *N*″-trimethyl-1,4,7-triazacyclononane.

The correlation between the M=O and M−L_{trans} bond length is also evident: the longer (weaker) the M=O bond, the weaker the *trans*-influence (the parameter Δ diminishes). Comparatively small variations in the lengths of the bonds between the metal and the *cis*-ligands are not regular in character.§

In the examples examined, the *trans*-ligand plays a relatively passive role: its bond with the metal is weakened to a greater or lesser extent in accordance with the requirements of the O−M multiple bond. The isomeric forms arising under these conditions can be naturally referred to as isomers of the metal−ligand multiple bond. Another very similar type of isomerism, in which the *trans*-ligand plays a more active role, is considered below in Section IV.

III. The choice of the *trans*-partner in complexes of d^0 and d^2 metals

The available structural data make it possible to establish series based on the preferential location in the *trans*-position relative to the oxo-ligand of ligands such as terminal halogen atoms, anionic *O*-organo-groups, water molecules, molecular *O*- and *N*-organo-donors, bridging halogen atoms, and asymmetric bridging oxygen atoms. For d^0 metals, the series assumes the following form:

$$Cl-,\ Br-,\ I-,\ RO-,\ R_2N-<H_2O\rightarrow,\ O_L\rightarrow,\ N_L\rightarrow,$$
$$-Cl_M\rightarrow,\ -R_2N\rightarrow<\rightleftarrows O_M\rightarrow,\ F-<-F_M\rightarrow,\ \rightleftarrows F_M\rightarrow.$$

The halogen atoms (Cl, Br, I), occupying the *trans*-position relative to the oxo-ligand, give way to water molecules and any neutral donor *O* and *N*-ligands; bridging donor oxygen atoms, forming a multiple bond with another metal atom, are even more preferable.

The exact position of the weakly polarisable F^- anion is not evident, since, so far as we are aware, the available structural data are restricted to only one example—the compound $(NH_4)[VO(O_2)\cdot F_2(bipy)]\cdot 2H_2O$.[16] In this complex, obtained by the reaction of $(NH_4)[VO(O_2)_2(bipy)]\cdot 4H_2O$ with HF, an inner-sphere rearrangement takes place in addition to the replacement of one peroxo-group in the initial compound by two fluorine atoms. The rearrangement consists in the migration of the axial N atom of the bidentate bipyridyl (bipy) ligand, in the *trans*-position to the oxo-ligand, to the equatorial position and the substitution of this position by one of the fluorine atoms. Thus in the given instance the fluoro-ligand in the *trans*-position to the oxo-ligand is preferable to the neutral donor nitrogen atom of bipy.

In addition, attention may be drawn to the fact that in the numerous hydrates of molybdenum oxide fluorides [not only Mo(VI) but also Mo(V) and Mo(IV)], the water molecules are not as a rule incorporated in the inner sphere of the complex and the inner sphere of a purely fluoride type. When the number of terminal fluorine atoms is insufficient, oligomerisation or polymerisation takes place more readily than the incorporation of a solvent molecule in the inner sphere. Of the two types of fluoride anions, the bridging

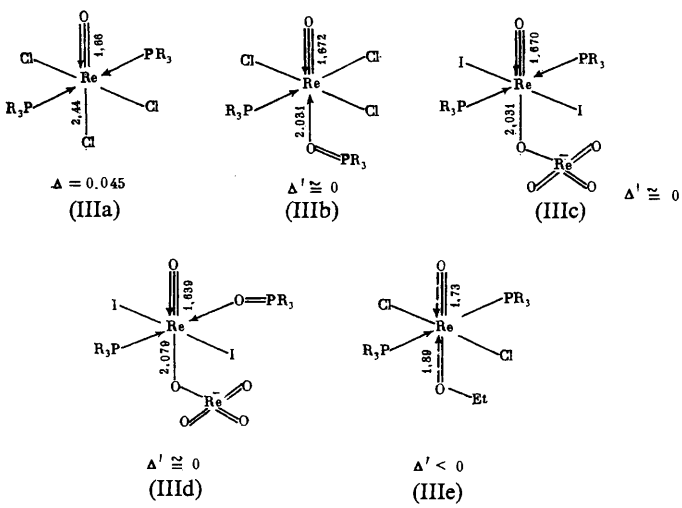
§The authors of a structural study of the green form of $(PPh_4)_2\cdot[MoO(CN)_4(H_2O)]\cdot 4H_2O$ [12] found that the Mo−$(H_2O)_{trans}$ bond length is 2.96 Å (this actually means that the coordination number of the metal is five). This result is very doubtful bearing in mind that the given compound is isotypical (pseudo-isostructural) with the compound $(AsPh_4)_2[MoO(CN)_4(H_2O)]\cdot 4H_2O$.[12] It is difficult to suppose that the difference between the Mo−H_2O distances, amounting to 0.5 Å, is caused by the different degrees of involvement of the water molecule in the hydrogen bonds or by the replacement of the cation PPh_4^+ by $AsPH_4^+$. It is apparently a result of the poor quality of the crystals employed and the low accuracy of the investigation, which was noted by the authors themselves.[12]

$-F_b\rightarrow$ or $\overleftarrow{=}F_b\rightarrow$ anion is preferable to the terminal F^- anion as the *trans*-partner of the multiple bond-linked ligand ($O\overleftarrow{=}$ or $-O\overrightarrow{=}$).

Overall, in the series presented above the trans-length parameter $\Delta(\Delta')$ increases from left to right and the self-consistency principle is satisfied:[17] the ligand whose σ-bond with a d^0 metal can be most readily weakened, i.e. the least polarisable [least "hard" according to Pearson[18]] donor among all the ligands present in the complex, enters most readily the *trans*-position relative to the multiple bond.

Initially it seemed that this principle is general and applies to not only d^0 metals but also to d^2 metals. Mixed halogeno-phosphine oxo-complexes are well known for Re(V) and Mo(IV). Structural studies have shown that phosphine, a powerful σ-donor, never occupies the *trans*-position relative to the multiple bond involving oxygen (the π-acceptor properties of PR_3 play no role) and gives way to a halogen (Cl, Br, I), for example, in the structure of *trans*-[$ReOCl(PEt_2Ph)_2$] (IIIa).[19]

It is just as natural that the halogen (Cl, Br) gives way to L_{trans}, which is a neutral oxygen-containing ligand—phosphine oxide in the complex [$ReOCl_3(OPPhEt_2)(PPhEt_2)$] (IIIb)[20]—and passes to the *trans*-position relative to PR_3. In the complex [$ReO(ReO_4).I_2(PPh_3)_2$] [11] containing two acido-ligands (iodine and perrhenate), ReO_4^- occupies the *trans*-position relative to the oxo-ligand [compound (IIIc)]. This can be regarded as evidence that the less-electron-donating ReO_4^- is preferred to the readily polarisable I^-, i.e. can be treated as a revision of the left-hand part of the series presented above. However, the perrhenate ligand occupies the same *trans*-position also in the complex [$ReO(ReO_4)I_2(OPPh_3)(PPh_3)$] (IIId),[11] containing also the neutral phosphine oxide ligand. Thus, in the case of Re(V) the singly-charged acido-ligand ReO_4 is preferable to the neutral phosphine oxide in the *trans*-position relative to O(oxo).



Furthermore, the *trans*-weakening Δ′ in the *trans*-preference series for d^2 metals does not increase from left to right, as for d^0 metals, but diminishes (regardless of the Re≡O multiple bond length). The *trans*-position relative to the oxo-ligand in the structure [ReO(OEt).$(PPh_3)_2Cl_2$] (IIIe)[20,21] is also occupied by an acido-ligand (the ethoxy-group) having one unpaired electron. Here Δ′ is altogether negative (it is smaller by 0.15 Å than the sum of Pauling's covalent radii of Re and O), i.e. the $M-L_{trans}$ bond is shortened (strengthened) and not lengthened (the Mo=O bond with the terminal oxo-ligand is simultaneously lengthened).

The reason for such "anomalous" choice of the *trans*-partner in the d^2 complexes becomes understood if one recalls that, in contrast to the complexes of d^0 metals, the multiple bond-linked ligands in these compounds always occupy opposite and not neighbouring vertices of the octahedron (see Fig. 1). Hence follows the conclusion that the ethoxy-group can also be regarded as a multiple bond-linked ligand¶.

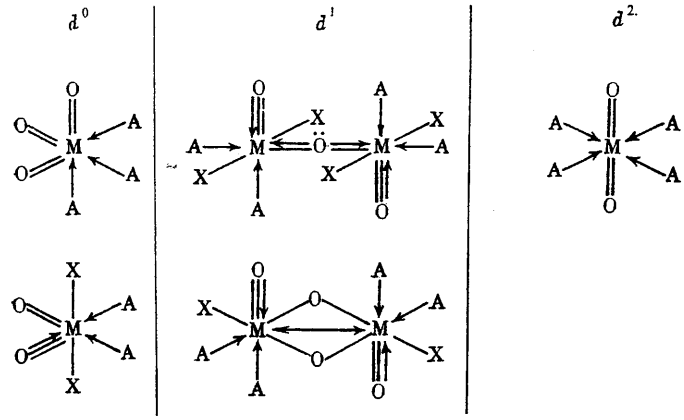
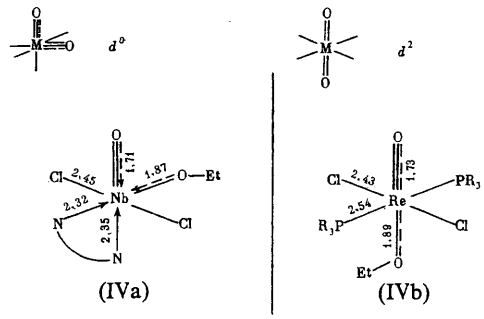


Figure 1. The disposition of multiple bond-linked ligands in the oxo-complexes of d^0 and d^2 Group V–VII transition metals.

This conclusion is well illustrated by the comparison of complexes of the d^0 metal Nb(V) and the d^2 metal Re(V): [NbO(OEt).(bipy)Cl_2] (IVa)[23] and [$ReO(OEt)(PPh_3)_2Cl_2$] (IVb).[20,21]



In complex (IVa), the ethoxy-group is in the *cis*-position relative to the O(oxo) atom and the Nb–O (OEt) distance (1.87 Å) is significantly smaller than the usual value, while in complex (IVb) the group is located in the *trans*-position relative to the O(oxo) atom at approximately the same distance from the metal. The Nb–O (OEt) and Re–O (OEt) distances are shorter by 0.20 and 0.13 Å

¶ The conclusion that the M–OEt bond is multiple was first reached from NMR data.[22]

respectively than the standard ("expected") M–OR bond lengths (2.07 and 2.02 Å respectively[4]). The increased multiplicity of the Nb–O (OEt) bond is also indicated by the Nb–N distances to the nitrogen atoms of bipyridyl: they are greatly lengthened (to approximately the same extent) in the *trans*-positions relative to both the multiple bond-linked oxygen and to the ethoxy-group (to 2.35 and 2.32 Å respectively).

The location of the ethoxy-group in the *trans*-position relative to the M=O bond and the shortening of the M–O(OEt) bond in the Re(V) complexes is not fortuitous, which is indicated by the geometrical parameters of the O⇶Re⇀ OEt fragment in all four structures investigated having the general formula $[ReO(OR)]X_2L_2$ (X = halogen)[20,21,24,25] (Table 2). In all these compounds, the OR^- (R = Et, Me) group is in the *trans*-position relative to the oxygen atom and in all cases the length of the bond between the Re atom and the methoxy- and ethoxy-groups is shortened (to 1.859 to 1.896 Å)‡. For comparison Table 2 presents the geometrical parameters of the O⇶Re–$OReO_3$ linkage in two complexes with the perrhenate group in the *trans*-position relative to oxygen.[11] The Re–O(ReO_4) *trans*-bond in $[ReO(ReO_4)I_2(PPh_3)_2]$ and $[ReO(ReO_4)\cdot(OPPh_3)(PPh_3)I_2]$ is lengthened to 2.031 and 2.079 Å respectively. The difference between the Re–O (OEt) and Re–O (ReO_4) bond lengths is quite natural (Fig. 2). While the π-electrons of the oxygen of the OR^- group can participate in the formation of a bond with the central rhenium atom, the similar electrons of the oxygen in the perrhenate anion are involved to a considerable extent in the molecular orbitals of the ReO_4^- anion itself and participate to only a slight extent in the formation of a bond with the central atom.

If the *trans*-ligand is a pure σ-donor, then the self-consistency principle operates: the *trans*-position relative to the oxo-oxygen atom is occupied preferentially by the hardest donor with a simultaneous increase in the length of the *trans*-bond. However, if the complex contains a ligand capable of π-donation to the metal, then in the case of a d^2 metal precisely this ligand occupies preferentially the *trans*-position relative to the oxygen-ligand and the *trans*-shortening via the π-mechanism is then superimposed on the *trans*-lengthening via the σ-mechanism, and the former may predominate.

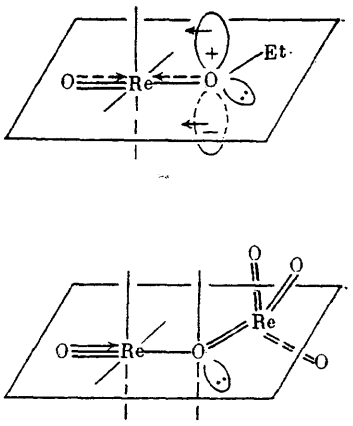


Figure 2. The structure of the ORe(OEt) and ORe(ReO_4) fragments in the mixed halogeno-phosphine monoxo-complexes of d^2-Re(V).

Table 2. Geometrical parameters of the MO(OR) (R = Me, Et, ReO_3) fragment in the Re(V) and Tc(V) d^2-complexes.

Compound	Bond lengths, Å		Refs
	O⇶M	M⇀OR_{trans}	
$ReO(OEt)Cl_2(PPh_3)_2$	1.73	1.89	[16, 17]
$ReO(OEt)I_2(PPh_3)_2$	1.715	1.880	[20]
$ReO(OMe)I_2(PPh_3)_2$	1.698	1.859	[20]
$ReO(OEt)Cl_2(Py)_2$	1.684	1.896	[21]
$TcO(OEt)Br_2(NPy)_2$	1.684	1.855	[22]
$ReO(OReO_3)I_2(PPh_3)_2$	1.670	2.031	[11]
$ReO(OReO_3)(OPPh_3)I_2(PPh_3)$	1.639	2.079	[11]

The following hypothesis may be put forward on the basis of the characteristic features of the stereochemistry of the complexes of d^0 and d^2 metals examined. Two opposite tendencies may be superimposed in the selection of the *trans*-partner and in the structural manifestation of the *trans*-influence in the case of oxo-complexes of a d^2 metal.

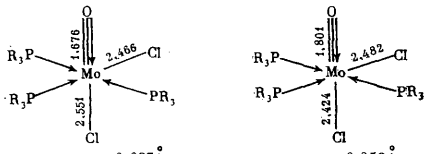
† The pentavalent technetium complex d^2-$[TcO(OEt)Br_2\cdot(NPy)_2]$ complex has a similar structure:[26] the Tc–O (OEt) bond in the *trans*-position relative to the Tc=O bond is shortened to 1.855 Å (the Tc=O bond length is 1.684 Å).

IV. The *trans*-influence isomerism in mixed halogeno-phosphine complexes of d^2 metals

In 1970, Butcher and Chatt[27] synthesised a series of diamagnetic mixed complexes of tetravalent molybdenum having the composition $MoOX_2(PR_3)_3$, where X is a halogen or a pseudo-halogen and PR_3 is a tertiary phosphine ligand. Depending on the individual characteristics of the ligand X and the nature of the substituents R, the two series of compounds obtained differed in colour. The series A complexes with X = NCO or NCS and PR_3 = $PPhMe_2$ or $PPhEt_2$ were blue, while the series B complexes with X = Cl, Br, or I and PR_3 = $PMePh_2$ or $PEtPh_2$ were green. As a rule, the stretching vibration frequency ν(Mo=O) in the series A complexes was higher by 5–10 cm^{-1} than in the series B complexes. Other characteristics, especially the ^1H NMR spectra[28] and the ^{95}Mo NMR spectra[29] of compounds of both series, were virtually indistinguishable. However, it was shown subsequently[30,31] that both the colour and the ν(Mo=O) frequency are not decisive parameters for the assignment of the compound to a particular series.

In two cases, for X = Cl and PR_3 = $PPhMe_2$ and for X = Cl and PR_3 = PMe_3, two isomers were obtained in each instance.[27] The isomers of the first of these compounds, $MoOCl_2(PPhMe_2)_3$, differed both in colour and in the μ(Mo=O) frequency [ν(MO=O) = 954 cm^{-1} for the blue isomer and 943 cm^{-1} for the green isomer]. The unstable green isomer was irreversibly converted into the stable blue isomer on heating in organic solvents. The authors[27] assumed that the different colours are due to the geometrical isomerism of the complexes: it was postulated that the *trans*-position relative to the oxo-oxygen atom is occupied by X in the series A complexes and by

PR_3 in the series B complexes. However, X-ray diffraction studies on the blue isomer of $MoOCl_2(PPhMe_2)_3$ (Va) [32] and on the unstable green isomer of $MoOCl_2(PPhEt_2)_3$ (Vb) [33,34] showed that they both have the *cis*-meridional geometry as regards to the disposition of the C atoms (one of the Cl atoms is in the *trans*-position relative to the oxo-oxygen atom).



However, the principal difference between the isomers consists in the unequal lengths of the bonds along the $O=Mo-Cl_{trans}$ coordinate: the multiple bond in the blue complex ($PR_3 = PPhMe_2$) is shorter than in the green complex ($PR_3 = PPhEt_2$) by 0.125 Å and instead of the *trans*-lengthening of the $Mo-Cl_{trans}$ bond in the blue complex, the bond undergoes *trans*-shortening in the green complex ($\Delta = +0.087$ and -0.058 Å respectively). The crystal structure of the green isomer $MoOCl_2(PPhMe_2)_3$ has been recently determined (at −160 °C [35]). As in the green $MoOCl_2(PPhEt_2)_3$, the Mo−O bond in this compound is greatly lengthened and its length is 1.80(2) Å. Other geometrical parameters of the complex are not quoted; only structural disorder, reducing the accuracy of the study, is noted.

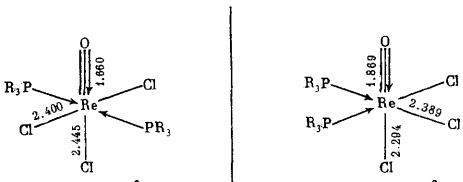
Thus, in compounds of this class the isomerism of the multiple metal−ligand bond is manifested in the sharpest and most clear-cut form: a shortening and not a lengthening of the *trans*-bond corresponds to the second isomer. It is quite evident that the bond with the *trans*-partner also plays an active role in the given instance in the formation of the second isomer. The negative parameter Δ ("*trans*-fixation") can be most naturally accounted for by the replacement of the pure $M-L_{trans}$ σ-bond by a multiple bond with a significant contribution by the π-donor component $M \rightleftarrows L_{trans}$, which is consistent with the tendency of the complexes of d^2 metals towards a *trans*-disposition of their multiple bond-linked ligands. This variety of the multiple bond isomerism can therefore be conveniently designated as the isomerism of the mutual influence of the ligands or the isomerism of axial π-bonding.

Some workers refer to differences of this kind between the structures of the complexes as "distortion isomerism". This name appears inappropriate: it is too indefinite and can include effects of a completely different nature [for example, the distortion of the Cu(II) octahedra induced by the Jahn−Teller effect or the distortion of the octahedra of the d^{10} metals Ag(I), Hg(II), Ga(III), and Sn(IV) caused by the hypervalence of the equatorial bonds].

Henceforth we shall refer to complexes with a short $Mo \equiv O$ bond and a greatly weakened $Mo-L_{trans}$ bond as A-isomers and to complexes with a longer Mo=O bond and a shortened $Mo=L_{trans}$ bond as B-isomers.

The crystal structures of a further two compounds of the class considered were determined in 1987: $MoO(NCO)_2(PPhEt_2)_3$ and $MoOCl_2(PMePh_2)_3$.[30] Although the former has a blue colour and the latter is green, it was found that both are A-isomers: their Mo=O distances are virtually the same (1.684 and 1.667 Å respectively), while the opposite $Mo-L_{trans}$ bonds are as usual lengthened as a consequence of the *trans*-influence ($\Delta_{av} = +0.085$ and $+0.043$ Å respectively).

We observed the *trans*-influence isomerism also in compounds of another d^3 metal, namely rhenium(V).[19,31] A structural study of two $ReOCl_3(PPhEt_2)_2$ isomers, having different colours, showed that they differ not only in the Re=O and $Re-Cl_{trans}$ bond lengths but also in the relative disposition of the Cl and PR_3 ligands in the equatorial plane. The green form (VIa)[19] is a meridional (with respect to Cl atoms) *trans*-isomer and at the same time a mutual *trans*-influence A-isomer, while the blue form (VIb)[31] is a facial (with respect to Cl atoms) *cis*-isomer and at the same time a mutual *trans*-influence B-isomer.



The short Re=O bond is lengthened by 0.209 Å on passing from the first isomer to the second, while the $Re-Cl_{trans}$ bond is shortened by 0.151 Å ($\Delta = +0.045$ and -0.095 Å respectively). The equatorial $Re-Cl_{cis}$ bonds have similar lengths in both isomers (their average values are 2.400 and 2.389 Å).

A stronger $Re-Cl_{trans}$ bond in the blue isomer compared with the green isomer is consistent with their different behaviour in solution.[36] Refluxing of the green *trans*-$[ReOCl_3(PPhEt_2)_2]$ isomer in alcohol leads to the ready substitution of the chloride ion in the *trans*-position relative to the oxo-ligand and to the formation of the violet complex *trans*-$[ReO(OR)Cl_2(PPhEt_2)_2]$. On the other hand, refluxing of the blue *cis*-$[ReOCl_3(PPhEt_2)_2]$ in methanol even for several days does not lead to methanolysis—the strong $Re-Cl_{trans}$ bond is not ruptured and the chloride ion occupying the *trans*-position relative to the oxo-oxygen atom is not substituted by the OMe^- group. However, on heating to 160 °C in the crystalline state, the blue complex is irreversibly converted into the green complex (the *cis* → *trans* and B → A isomerisations take place simultaneously).

The authors[30] believe that the colour of the compounds of the class considered is determined by the basicity of the ligands X and PR_3: the blue complexes contain more basic ligands X and PR_3 ($X = NCS^-, NCO^-$, $PR_3 = PMe_3, PPhMe_2, PPhEt_2$), while the green complexes contain the less basic ligands ($X = Cl, Br, I$; $PR_3 = PMePh_2, PEtPh_2$). A combination of ligands of different basicity gives rise to the possibility of the coexistence of the blue and green isomers. This applies, in particular, to the combination X = Cl and $PR_3 = PPhMe_2$ or PMe_3.

The M−L bond lengths, the *trans*-influence parameters Δ, the differences between the M=O bond lengths in the two isomers $\Delta_{M=O}$, and the stretching vibration frequencies ν(M=O) for certain halogeno-phosphine complexes are listed in Table 3. It follows from these data that a complete correlation is not observed between the colour, the frequencies ν(M=O), and the parameter Δ. The colour and the frequencies ν(M−O) can be regarded as correlated for only two forms of the same compound: the higher and lower frequencies correspond respectively to the blue and green forms (the first two pairs in Table 3). On the other hand, if the complexes are different, then the absolute values of ν(M=O) even for compounds with similar compositions are not correlated with colour. In

Table 3. Geometrical parameters and vibration frequencies ν(M=O) of the *trans*-influence isomers of mixed halogeno-phosphine complexes of d^2 metals.

Compound	Isomer	Colour	Bond lengths, Å			Δ, Å	$\Delta_{M=O}$*, Å	$\nu_{M=O}$, cm^{-1}	Refs.
			M=O	M−L_{trans}	M−L_{cis}				
trans-[$ReOCl_3(PPhEt_2)_2$] *cis*-[$ReOCl_3(PPhEt_2)_2$]	A B	Green Blue	1.660 1.869	2.445 (Cl) 2.294 (Cl)	2.400 (Cl) 2.389 (Cl)	+0.045 −0.095	0.209	975 986	[18, 19, 37] [31, 37]
cis-$MoOCl_2(PPhMe_2)_3$	A B	Blue Green	1.676 1.80	2.551 (Cl) — (Cl)	2.464 (Cl) — (Cl)	+0.087 —	0.124	954 943	[27, 32] [27, 35]
cis-$MoOCl_2(PPhEt_2)_3$	B	Green	1.801	2.424 (Cl)	2.482 (Cl)	−0.058	—	940	[27, 34]
cis-$MoOCl_2(PMePh_2)_3$	A	Green	1.667	2.509 (Cl)	2.466 (Cl)	+0.043	—	945	[27, 30]
cis-$MoO(NCO)_2(PPhEt_2)_3$	A	Blue	1.684	2.180 (NCO)	2.095 (NCO)	+0,085	—	940	[27, 30]

*$\Delta_{M=O}$ is the difference between the M=O bond lengths in the two isomers ["blue"−"green" for Re(V) and "green"−"blue" for Mo(IV)].

particular, ν(Mo=O) for the blue complex *cis*-$[MoO(NCO)_2.(PPhEt_2)_3]$ is located in the region characteristic of the green isomers of the mixed halogeno-phosphine complexes of molybdenum (IV).

The correlation between the colour and sign of Δ is still weaker. Not only the blue forms *cis*-$[MoOCl_2(PPhMe_2)_3]$ and *cis*-$[MoO(NCO)_2(PPhEt_2)_3]$ but also the green forms *cis*-$[MoOCl_2.(PPhMe_2)_3]$ and *trans*-$[ReOCl_3(PPhEt_2)_2]$ belong to type A (positive Δ), while type B (negative Δ) includes not only the green forms *cis*-$[MoOCl_2(PPhEt_2)_3]$ and *cis*-$(MoOCl_2(PPhMe_2)_3]$ but also the blue form *cis*-$[ReOCl_3(PPhEt_2)_2]$. In essence, the blue and green forms of the Re(V) complexes considered [and the ν(Re−O) frequency characteristics] change places: the green form with the lower ν(Re=O) frequency corresponds to the A-isomer and the blue form corresponds to the B-isomer.

The absence of a complete correlation between the length of the M=O double bond and its stretching vibration frequency, mentioned above, is somewhat unexpected. It shows that the ν(Mo=O) frequency is not characteristic: it clearly depends on fine nuances of the composition of the compound as a whole.

Furthermore, the type of the *trans*-influence isomer is determined not by the basicity of the entire set of ligands but by the basicity and capacity for π-donor interaction with the metal of the L_{trans} ligand: its relatively low donor capacity is due to the stability of the A-isomer and its tendency towards π-donation promotes the transition to the B-form. Chlorine satisfies both these requirements. Depending on the conditions, it can either virtually not participate or can significantly participate in π-donation to the metal.

Summarising the foregoing, we may note two factors. Firstly, the *trans*-influence isomerism is determined by the distribution of the σ- and π-interactions along the O=M−L_{trans} coordinate. Within the framework of the limiting canonical forms, the A-isomer can be written as O≡M−L_{trans}, while the B-isomer can be formulated as O=M≡L_{trans}. In essence, the O−M bonds in the compounds $[MoOCl_2(PPhEt_2)_3]$ (Vb) and *cis*-$[ReOCl_3(PPhEt_2)_2]$ (VIb) should be regarded as double bonds and not as triple bonds, while the M−Cl_{trans} bonds should be regarded as double bonds and not as single bonds, i.e. the axial π-bonding isomerism obtains.

The above examples show that the chlorine atom can function also as the usual σ-acido-ligand and under certain conditions as a multiple bond-linked ligand (with a significant involvement in π-donation).

Secondly, the preferential formation of a particular *trans*-influence isomer (and the corresponding redistribution of electron density along the axial coordinate) depend under certain conditions not only on nuances in composition but also on the characteristic features of the disposition of the remaining ligands (Re complexes).

One cannot rule out the possibility that the transition from one isomer to another in the acido-phosphine anionic or cationic complexes, for example, $[Mo^{IV}OCl_3(PR_3)_2]^-$ or $[Re^{V}OCl_2(PR_3)_3]^+$, can be determined also by the nature of the outer-sphere ion or even by the presence or absence of the molecules of water of solvation, as in the case of the anionic Mo(IV) complexes $Kat_2[MoO(CN)_4.(H_2O)].nH_2O$ examined above.

V. Analysis of the disposition of the chelate organic ligands in oxo-complexes of d^0 and d^2 metals

We shall consider yet another important aspect of the choice of the *trans*-partner of the oxo-ligand in the complexes of d^0 and d^2 metals. This concerns the disposition in the oxo-complexes of anionic chelate ligands having acido- (X^-) and neutral-donor (A) coordinatively active atoms.

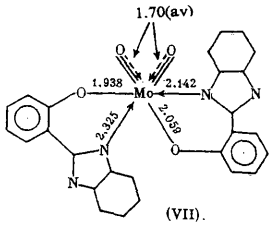
For d^0 metals, this problem has been solved unambiguously, fully in conformity with the principle of self-consistency. The *trans*-position relative to the multiple bond always contains the neutral-donor "end" of the chelate ligand A, whose lone electron pair "adjusts" readily to the requirements of the *trans*-active multiple bond-linked ligand. The structures of the molybdenum(VI) dioxo-complexes with hydroxamic acid anions containing different solvating molecules, i.e. $MoO_2L_2.A$, may serve as examples. Here HL = PhCoNHOH and A = MeCOEt,[38] $^2/_3$EtCOOH,[39] and Bu^nOH[40] or HL = HOC_6H_4CONH and A = $2H_2O$.[41] Their *trans*-positions relative to the oxo-ligands are occupied by the donor atoms of the

Table 4. Geometrical parameters of the d^2-M(V) (M = Re, Tc) monoxo-complexes with bidentate (O, N) and tridentate (O, N, O) organic ligands.

Compound*	Bond lengths, Å			Δ, Å	Refs.
	M=O	$M-O_{trans}$	$M-N(O)_{cis}$		
ReOCl (Me-Sal)$_2$	1.680	1.976	1.995 (O), 2.111(N)$_{av}$	−0.019	[45]
trans-[ReOCl$_2$(PPh$_3$)(Me-Sal)]	1.701	1.949	2.125 (N)	—	[47]
cis-[ReOCl$_2$(PPh$_3$)(Me-Sal)]	1.660	1.955	2.150 (N)	—	[47]
trans-[ReOBr$_2$(PPh$_3$)(Ph-Sal)] (tricl.)	1.680	1.972	2.141 (N)	—	[48]
trans-[ReOBr$_2$(PPh$_3$)(Ph-Sal)] (monocl.)	1.683	1.937	2.173 (N)	—	[49]
[ReOCl$_2$(PPh$_3$)]$_2$ (μ-Salen)·CHCl$_2$	1.680	1.925	2.150 (N)	—	[50]
TcOCl (Ph-Sal)$_2$	1.67	1.94	1.99 (O), 2.155(N)$_{av}$	−0.05	[46]
ReOCl$_2$(PPh$_3$){PhC (O)NNCMe$_2$}	1.685	2.013	2.130 (N)	—	[53]
TcOCl (ONC$_9$H$_5$Me)$_2$	1.649	1.994	1.947 (O), 2.197(N)$_{av}$	+0.047	[54]
TcO (ONC$_9$H$_6$) (O$_2$NC$_{13}$H$_{19}$)	1.659	2.014	2.007(O)$_{av}$, 2.130(N)$_{av}$	+0.007	[55]

Notation: Sal = salicylideneaminate; Salen = ethylenebis- (salicylideneaminate).

ligand O(C), while the *cis*-positions are occupied by the acido-atoms O(N). In all these and other oxo-complexes of d^0 metals‡ the *trans*-lengthening is as a rule 0.15−0.30 Å. We are aware of only one example of the infringement of this general rule governing the orientation of the acido-donor chelate ligand in d^0 metal complexes. In the structure of [Mo^{VI}O$_2$L$_2^{(2)}$].2EtOH (VII),[44] where $L^{(2)}$ = 2-*o*-hydroxyphenylbenzimidazole, the two chelate *O, N*-ligands $L^{(2)}$ are coordinated to the metal in different ways.

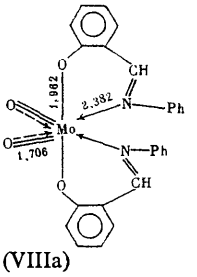


Δ_O = + 0.121Å
Δ_N = + 0.183Å

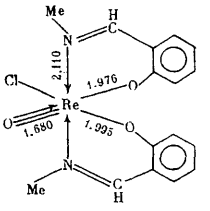
(VII).

One of them is coordinated in the usual way—the neutral donor N atom is located in the *trans*-position relative to the multiple bond, while the other ligand is "rotated", as a result of which the acido-"end" of $L^{(2)}$, i.e. the O atom, is in the *trans*-position relative to the second oxo-oxygen atom. Both ligand−metal bonds, occupying *trans*-positions relative to the M=O bonds, are weakened under these conditions albeit to different extents. The quantity Δ is +0.183 Å for the Mo−N bond and +0.121 Å for the Mo−O bond. The reason for the rotation of one of the ligands $L^{(2)}$ is not evident. Possibly it is associated with the way in which the complex is obtained. One should also draw attention to the fact that the M−L_L bond in the first of the two ligands, occupying the third *cis*-position relative to both M=O bonds, is also significantly shortened (to 1.938 Å), i.e. is in essence also multiple. Therefore the preference for one orientation over another possible orientation is not all that important for the second chelate ligand: at any rate, the N_L atom is in the *trans*-position relative to the M=O or M⇄O_L multiple bond.

We may quote yet another example of the disposition of the chelate ligand typical for the oxo-complexes of d^0 metals. In the silicylideneanilinato-complex [MoO$_2$(Ph-Sal)$_2$] (VIIIa) which we investigated[43] both chelate ligands are oriented in accordance with the requirements for self-consistency: the *trans*-positions relative to the multiple bonds contain the donor "ends" of the chelates (the imine N atoms), while the *cis*-positions contain the acido-"ends" (the hydroxyl O atoms). The *trans*-lengthening Δ′ is on average 0.21 Å.



(VIIIa)



(VIIIb)

This example is especially interesting when compared with the isotypical complexes of d^2 metals [Re(V) and Tc(V)]:[ReOCl.(Me-Sal)$_2$] (VIIIb)[45] and [TcOCl(Ph-Sal)$_2$].[46] Comparison of these complexes makes it possible to reveal clearly the differences in the coordination of chelate monoionic ligands in d^0 and d^2 complexes. Firstly, the chelate ligand is "rotated": the acido-O atom of the ligand R-Sal moves to the *trans*-position relative to the multiple bond in the d^2 complexes. Secondly, the *trans*-lengthening in the complexes of d^0 metals is replaced in the case of d^2 metals by a

‡A complete compilation of the geometrical parameters of monomeric octahedral molybdenum complexes with chelate ligands and Mo−O and Mo−N bonds occupying *trans*-positions relative to Mo=O has been published.[42,43]

slight but clearly manifested *trans*-shortening of the M–O(Sal) bonds [in the given instance by 0.019 and 0.05 Å respectively in the Re(V) and Tc(V) complexes].

This result is not fortuitous, since the same feature is characteristic of a whole series of monomeric octahedral d^2-Re(V) complexes of a similar composition incorporating R-Sal ligands[47–49] (Table 4). In all these structures the *O, N*-chelate ligands are coordinated to the metal in a similar manner (the acido-O atom occupies the *trans*-position, while the donor N atom occupies the *cis*-position relative to O_{oxo}), i.e. a "rotation" is observed compared with the complexes of d^0 metals. In particular, out of the seven theoretically possible isomers of [ReOCl(PPh$_3$)(Me-Sal)] (Fig. 3), only two have been isolated in the crystalline state—the *cis*- and *trans*-isomers (A) and (B)—and in the structures of both an O (and not N) atom of the Me-Sal ligand is in the *trans*-position relative to the oxo-oxygen atom.[47] Exactly the same situation is obtained in the conformational isomers of *trans*-[ReOBr$_2$(PPh$_3$)(Ph-Sal)],[48,49] where the *trans*-position relative to the O (oxo) atom is occupied by the O (Ph-Sal) atom, while the N (Ph-Sal) atom is in the *trans*-position relative to the phosphine ligand.

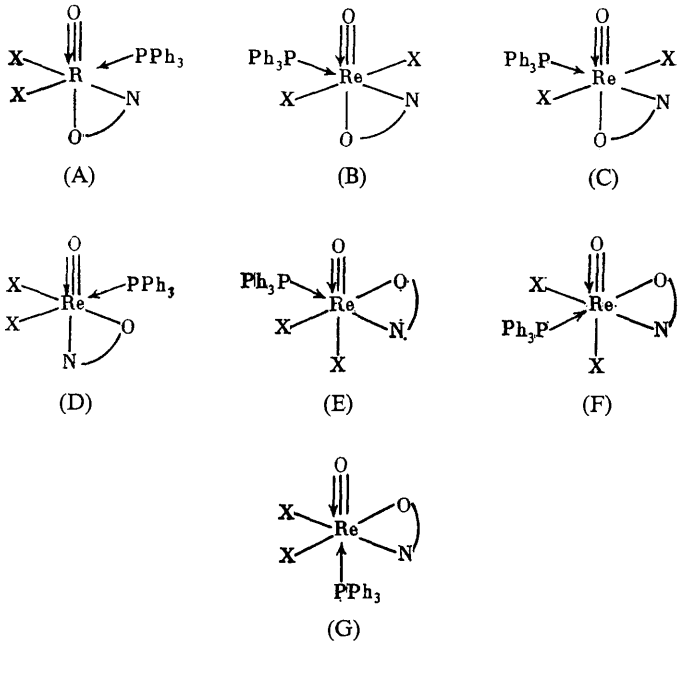
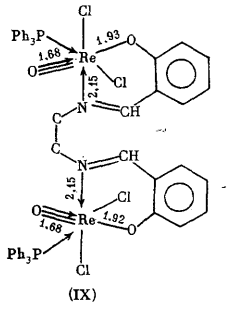


Figure 3. The theoretically possible geometrical isomers of the d^2-Re(V) complexes of the type ReOX$_2$(PPh$_3$)(R-Sal), where X = Cl or Br and R = Ph or Me.

The reason for this is fairly evident. The oxygen atom linked directly to the benzene ring is a conductor of the π-interaction from the ring to the metal, while the nitrogen atom, separated from the unsaturated group by the CH_2 group is not such a conductor. Accordingly, the M–O(Sal) bond in the complexes of d^0 metals is located in the *cis*-position, while in the complexes d^2 metals it is in the *trans*-position relative to the M=O bond.

It is seen from Table 4 that the R–O (chelate) bond, *trans* to Re=O, is on average shorter by 0.03 Å in six complexes than the only Re–O (chelate) bond *cis* to Re=O in the compound [ReOCl.(M-Sal)$_2$];[47] at the same time, the length of these bonds is smaller by the same amount than the standard Re–OH distance, which is 2.00 Å[4] (Δ' = 0.032 Å) and smaller by ~0.07 Å than the sum of the covalent radii of rhenium and oxygen (2.04 Å according to Pauling).

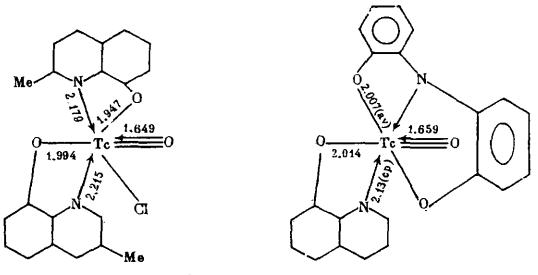
The Re–O (Sal) bond, in the *trans*-position relative to Re=O in the dimeric d^2-Re(V) complex [ReOCl$_2$(PPh$_3$)]$_2$(μ-Salen).CHCl$_2$ (IX), is shortened even more drastically.[50]



The length of this bond is on average 1.925 Å (Δ' = 0.075 Å). On the whole, the Re–O (Sal) distances (*trans* to Re-O) are in the range 1.925–1.976 Å (the mean is 1.963 Å) in the six d^2-Re(V) complexes containing salicylidene-aminato-ligands[45,47–50] and are on average somewhat shorter than the Re=O (Sal) distances (*trans* to Re–Cl) in the complexes *mer*-[Re^{IV}Cl$_3$(Ph-Sal)(PPhMe$_2$)] (1.970 Å)[51] and *cis*-[Re^{III}Cl$_2$(Ph-Sal)(PPhMe$_2$)$_2$] (1.990 Å).[52]

The same mode of coordination of the bidentate Ph-Sal with a similar shortening of the M–O (Sal) bond has been observed also in the pentavalent technetium compound TeOCl(Ph-Sal)$_2$:[46] the Tc–O (Sal) bond in the *trans*-position relative to Tc≡O (1.94 Å) is shorter by 0.5 Å than the analogous Tc–O (Sal) bond the second bidentate ligand.

In certain cases, the "rotation" of the ligand shifting the acido-centre to the *trans*-position relative to the multiple bond-linked ligand is not accompanied by a shortening of the M–L$_{trans}$ bond. This applies particularly to the complexes [ReOCl$_2$(PPh$_3$).{PhC(O)NNCMe$_2$}],[53] [TcOCl(ONC$_9$H$_5$Me)$_2$] (Xa),[54] and TcOL$^{(2)}$L$^{(3)}$ (Xb), where L$^{(2)}$ is the bidentate 8-hydroxyquinolinate ligand, while L$^{(3)}$ is the tridentate *N*-(2-oxidophenyl)salicylidenc-aminate ligand.[55]



In the first complex, the Re–O$_{trans}$ bond is 2.013 Å long, in the second complex (Xa) the Tc–O$_{trans}$ bond is 1.994 Å long (longer by 0.047 Å than the analogous Te–O$_{cis}$ bond of the second bidentate

ligand, while in the third complex (Xb) the $Tc-O_{trans}$ bond is 2.014 Å long (on average longer by 0.007 Å than both $Tc-O_{cis}$ bonds). However, in all three compounds the $M-O_{trans}$ distances do not exceed the standard length of the single bond in the hexacoordinate and heptacoordinate complexes (for example, the Tc–O bond length is 2.02 Å according to the data of Bandoli et al.[56]).

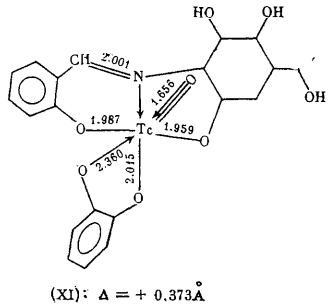
According to spectroscopic data (IR, ^{1}A NMR, and mass spectra), a further seven complexes having the general formula $Mo(L^{(3)})$ (R-Sal), where M = Tc or Re and R = H, Me, or Ph, have structures similar to those described above:[55] the phenolic (charged) oxygen atom of the bidentate salicylideneaminate ligand R-Sal is located in the *trans*-position relative to the O (oxo) atom.

Thus it follows from the foregoing that, in contrast to complexes of d^0 of metals, the *trans*-partner of the oxo-ligand in the d^2 complexes of Re(V) and Tc(V) is the acido-"end" (and not the neutral-donor "end") of the chelate ligand.

The authors of the original investigations[45–50, 53–55] apparently missed the importance of this result. To us there seems to be no doubt that it is a consequence of the simultaneous manifestation of the two tendencies described above—the set of σ-donor and π-dative properties of the ligand§. Therefore it is not to be expected that the analogous "rotation" of the chelate ligands in the complexes of d^2 metals will occur in all cases; everything depends on the possibility and degree of involvement of the acido-"end" of the chelate in bonding to the metal. Evidently the "rotation" should be a characteristic feature of unsaturated chelate systems. The degree of involvement of the chelate ligand's π-electrons in the formation of a bond with the metal can be inferred from the disposition of the chelate ligand in the oxo-complexes of d^2 metals and from the degree of shortening of the $M-O_L$ bond.

An example of a complex of a d^2 metal in which the *trans*-position relative to the M=O bond is occupied by the donor "end" of the chelate ligand may be provided by $TcOL^{(3)}L^{(2)}$, where $L^{(3)}$ is the dianion of *N*-salicylidine-D-glucosamine (Glusal) and $L^{(2)}$ is the monoanion of salicylaldehyde (Sla) (XI).[58]

In this compound, the carbonyl O atom of the Sla ligand is in the *trans*-position relative to the oxo-ligand, while the acidic phenolic O (Sla) atom occupies the *cis*-position relative to the Tc=O bond (in the *trans*-position relative to the N atom of the Glusal ligand).

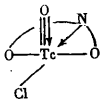


(XI): Δ = + 0.373Å

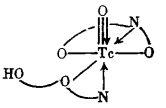
§One should recall the hypothesis that *trans*-dioxo-complexes of d^2 metals are formed only in the presence of ligands L which are pure σ-donors (weak π-donors), for example, in the presence of tetraazocyclotetradecane—the structure *trans*-$[Tc^VO_2(L)](ClO_4).H_2O$.[57] According to the authors,[57] the *trans*-TcO_2^+ compounds cannot be formed in the presence of salicyclidene-aminate ligands.

The $Tc-O_{trans}$ = 2.360 Å bond is greatly lengthened compared with the $Tc-O_{cis}$ bonds (1.959–2.015 Å): Δ = +0.373 Å. However, this example cannot be regarded as characteristic, since the phenolic oxygen atom is in principle a good conductor of the π-interaction and one may expect that it will in fact occupy the *trans*-position relative to the Tc=O bond.

The most probable cause of the reorientation of the ligand $L^{(2)}$ is believed[58] to be the specific features of the initial reaction occurring under the conditions of kinetic control. The complex [TcO(Glusal)(Sla)] was obtained by the reaction of $TcOCl_4^-$ with a fivefold excess of $GlusalH_2$ in methanol. The presence of the chelating ligand Sla in the final product is not the result of the hydrolysis of the ligand $Glusal^{2-}$ before coordination, since the direct reaction of $TcOCl_4$, $GlusalH_2$, and SlaH, taken in the stoichiometric proportions of 1:1:1, does not lead to the formation of [TcO(Glusal)(Sla)]. Furthermore, the initial reaction proceeds readily only in methanol (and also in ethanol but with a low yield), whereas in acetone, tetrahydrofuran (THF), and dimethyl sulphoxide (Me_2SO) it does not occur. According to the authors, the role of the solvent is very great: THF, Me_2SO, and actone promote the rapid hydrolysis of $GlusalH_2$ with formation of SlaH and glucosamine, whereas in methanol the ligand $GlusalH_2$ is stable for a long time. The authors suggest that the initial reaction can take place in stages with the successive addition of two $GlusalH_2$ ligands and the formation of two intermediates: the square-pyramidal [TcOCl(Glusal)] (XIIa) with the tridentate (O,N,O)-ligand $Glusal^{2-}$ in the plane of the base of the pyramid and the octahedral [TcO(Glusal)(GlusalH)] (XIIb) in which the bidentate ligand $GlusalH^-$ is coordinated to the acidic phenolic O atom in the *cis*-position and to the neutral N (imine) atom in the *trans*-position relative to the oxo-ligand.



(XIIa)



(XIIb)

This mode of coordination facilitates the direct addition of the ligand Sla^-, formed on hydrolysis of $GlusalH^-$, via the carbonyl O atom, since the Tc–N (Glusal) bond is weakened to the greatest extent.

Thus one can postulate that in the given instance the thermodynamically less favourable mode of coordination of the ligand Sla to the metal is determined by the reaction conditions.

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The data presented permit the conclusion that the problem of the relative disposition of the ligands in complexes containing multiple bond-linked ligands is far from being exhausted and that further studies may reveal many new and unexpected nuances both in the overall structure of the complexes and in the geometrical parameters characterising the mutual influence of the ligands. In particular, this concerns the complexes of d^2 metals whose structure is determined, judging from all the available data, by the combined effects of several opposed tendencies, including kinetic factors.

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The mechanism of the dehydration of alcohols and the hydration of alkenes in acid solution

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ABSTRACT. Kinetic data for the hydration of unsaturated compounds, the dehydration of alcohols, and the isotope exchange of the oxygen atom in alcohols and aqueous solutions of strong acids are analysed to establish the detailed mechanisms of these reactions. The catalytic action of the acid is caused not only by its ability to protonate the reactant but also by the possibility of the formation of reactive complexes of the reactant with the acid hydrates or the molecules of the undissociated acids. Equations are presented whereby the influence of the ionising capacity of the medium on the effective rate constants for the reactions indicated can be taken into account quantitatively. The question of the involvement of carbonium ions as reactive intermediates in reactions involving the dehydration of alcohols, the hydration of unsaturated compounds, and the isotope exchange of the oxygen atom in alcohols is examined. Complexes of the reactant with a solvated proton, the acid molecules, and the acid hydrates are the intermediates in these reactions. The relative contributions of the complexes to the effective rate constant depend on the acid concentration in the aqueous solution.

The bibliography includes 65 references

Contents

I. Introduction 63
II. Kinetics of the hydration of alkenes and of the dehydration of alcohols on the basis of the carbonium ion concept 64
III. A method for the determination of the mechanism of the dehydration of alcohols and the hydration of unsaturated compounds from kinetic data 67
IV. The mechanism of the exchange of the oxygen atom in alcohols and of the racemisation of optically active alcohols 74
V. Conclusion 76

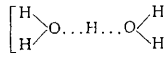
I. Introduction

The study of the detailed mechanisms of the strong acid-catalysed reactions involving the hydration of unsaturated compounds (UC) and the dehydration of alcohols (ROH) in aqueous solutions is of interest for the development of a theory of acid catalysis and for the quantitative estimation of the influence of the structure of organic substances on their reactivity. Systematic studies on the kinetics and the detailed mechanisms of these reactions were initiated at the beginning of the 1940s. Certain data on this question are contained in a monograph (Ref. 1, p. 210) and a review.[2]

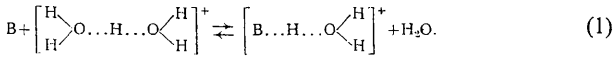
Judging from the kinetics, the dehydration of ROH and the hydration of UC in aqueous solutions are complex reactions. As a rule, the kinetic data were analysed previously from the concept that in aqueous solutions of strong acids a proton adds to the reactant base and that the protonated form is the intermediate reactive complex which can be formed either in the equilibrium stage or in the rate-limiting stage. This idea constitutes a gross simplification of the real picture of the complex interaction in solutions.

Many facts have now accumulated which make it possible to expand our knowledge about the nature of the ionising and catalytic action of acids.

Protonation is only one of the forms of ionisation in aqueous solutions of strong acids. Ionisation can entail the formation also of complexes of the base with the molecules of the undissociated acid and with the acid hydrates,[3] some of which may be reactive in the reactions investigated. It has been established that in aqueous solution, protons are present not as H_3O^+ ions but as $H_5O_2^+$ ions, which exist as a result of the formation of the strong hydrogen bond


(Ref.4)

Naturally, these ions are solvated by the solvent. Protonation in aqueous solution is a reaction involving the substitution of a water molecule in the $H_5O_2^+$ ion by the base B:


(1)

The protonated form BH_3O^+ is a complex of the base with the H_3O^+ ion, which also exists by virtue of the presence of a strong hydrogen bond.[5] The reaction products can be formed simultaneously via several pathways.

It is of interest to analyse the available literature kinetic data on the hydration of UC and the dehydration of ROH taking into account the ideas described above concerning the ionising capacity and catalytic activity of strong acids in aqueous solutions. This paper is in fact devoted to this problem. Valuable information about the detailed mechanisms of these reactions can be obtained from experimental data for the isotope exchange of the oxygen atom of the OH group in alcohols and the racemisation of optically active alcohols in acid media and also by measuring the isotope effects on replacement of a hydrogen atom by deuterium. These questions are examined in this review for this reason.

II. Kinetics of the hydration of alkenes and the dehydration of alcohols on the basis of the carbonium ion concept

Kinetic measurements are usually made using low concentrations of the UC and the ROH which do not affect the catalytic properties of the solution. In this case the UC hydration and the ROH dehydration reactions at constant acid concentration are first order relative to the concentration of the organic reactant. As a rule, these reactions are reversible:

$$R'-CH=CH_2+H_2O \underset{k_{dehydr}}{\overset{k_{hydr}}{\rightleftarrows}} R'-\underset{OH}{\underset{|}{CH}}-CH_3$$

and

$$-dc_{UC}/dt = dc_{ROH}/dt = k_{hydr}\,c_{UC} - k_{dehydr}\,c_{ROH}, \quad (2)$$

where k_{hydr} includes also a function characterising the concentration of water in solution.

Interpretation of the results of kinetic measurements carried out in a medium with a constant acid concentration yields the rate constant $k_{sum} = k_{hydr} + k_{dehydr}$. The equilibrium concentrations of the UC and of the alcohol obtained (c^{∞}_{UC} and c^{∞}_{ROH}) are measured for the separate determination of k_{hydr} and k_{dehydr}. According to Eqn. (2),

$$c^{\infty}_{ROH}/c^{\infty}_{UC} = k_{hydr}/k_{dehydr}.$$

It is noteworthy that most of the kinetic studies on the UC hydration and the ROH dehydration reactions have been carried using aqueous solutions of strong acids—sulphuric, perchloric, and nitric. The acidity functions H_0 and also the thermodynamic activities of the acid and water at 25 °C are known for such solutions. For sulphuric acid solutions, these quantities have been measured also at other temperatures.

An increase in the concentration of the strong acid in moderately concentrated and concentrated aqueous solutions leads to a sharp increase in k_{hydr} and k_{dehydr}. As a rule, a linear relation is observed between lg k_{hydr} and H_0:

$$\lg k_{hydr} + \alpha' H_0 = \text{const}. \quad (3)$$

The quantity α' is sometimes close to unity but in the vast majority of cases $\alpha' > 1$ and is in the range 1.1–1.4. The linear relation between lg k_{hydr} and H_0 can be explained by the formation of the protonated form of the alkene, which is regarded as the intermediate complex in the hydration of the UC. According to Whitmore,[6] this ion includes a positively charged carbon atom with six electrons:

$$R-CH=CH_2+H^+ \rightleftarrows R-\overset{+}{C}H-CH_3.$$

The Whitmore carbonium ion is a σ-complex.

The earlier studies on the kinetics and mechanism of the hydration of UC and the dehydration of ROH were devoted to the detection of the existence in acid solutions of Whitmore carbonium ions as intermediate reactive species. According to Whitmore, one of the ways of obtaining such carbonium ions involves the addition of a proton to the double bond of the UC. It is suggested that this reaction is reversible. It is also assumed that the reactions involving the elimination of an alkene from alkyl halides and alcohols are unimolecular and proceed via the same mechanism (Ref. 7, p. 540). In the case of alkyl halides, the reactant dissociates in the slow step into the carbonium ion and the anion X^-:

$$R_2CH-CR_2X \rightarrow R_2CH-\overset{+}{C}R_2 + X^-.$$

The step in which the carbonium ion decomposes into an alkene and a proton is rapid:[7]

$$R_2CH-\overset{+}{C}R_2 \rightleftarrows R_2C=CR_2 + H^+.$$

According to Whitmore,[6] as a result of the protonation of the ROH in the formation of an alkene from an alcohol in an acid a stable oxo-compound (the protonated form of the alcohol) is formed initially and then decomposes in the slow step into a carbonium ion and water:

$$CH_3CH_2OH + H^+ \overset{\text{fast}}{\rightleftarrows} CH_3-CH_2\overset{+}{O}H_2,$$

$$CH_3-CH_2OH_2^+ \overset{\text{slow}}{\rightleftarrows} CH_3-\overset{+}{C}H_2 + H_2O,$$

$$CH_3-CH_2^+ \overset{\text{fast}}{\rightleftarrows} CH_2=CH_2 + H^+.$$

As in the majority of the available publications, H^+ for simplicity is a solvated proton with solvation shell of indefinite composition and ROH_2^+ denotes the protonated form of the alcohol.

If the mechanisms of the formation of carbonium ions presented above do indeed occur and the ions have the properties attributed to them, then the following features due to the high reactivity of carbonium ions and their rapid equilibration with the UC in an acid medium should be manifested.

1. The hydration should be accompanied by the still more rapid isomerisation of one UC to another, provided that the same carbonium ion is formed on protonation.

2. In the presence of deuterium or tritium oxides in the medium, isotope exchange of the hydrogen atoms attached to the carbon atoms of the double bond of the UC should be observed. This exchange should precede the rate-limiting step of the hydration of the UC.

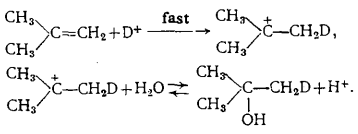
In order to observe the postulated effects, mainly aliphatic alcohols and the UC obtained from them have been used. As early as 1940, a study was published[8] from which it followed that, even if the Whitmore ions are formed, they are incapable of exchanging a hydrogen atom at the carbon atoms of the double bond: the dimer obtained on dimerisation of anethole in a solution of DCl in methanol contained no more deuterium than the initial monomer. Unfortunately, at the time this result did not receive due attention.

The study of the hydration in 0.973 M HNO_3 solution in water at 25 °C of the two isomeric alkenes 2-methylbut-2-ene and 2-methylbut-1-ene, from which the same carbonium ion should be formed on protonation, i.e.

$$\left.\begin{array}{l} H_3C-\underset{CH_3}{\underset{|}{C}}=CH-CH_3 + H^+ \\ H_2C=\underset{CH_3}{\underset{|}{C}}-CH_2-CH_3 + H^+ \end{array}\right\} \rightarrow CH_3-\overset{CH_3}{\overset{|}{\overset{+}{C}}}-CH_2-CH_3,$$

showed[9] that at 50% conversion of the UC into an alcohol there is no appreciable isomerisation of the initial alkene. The hydration of these alkenes results in the formation of only one product—t-pentyl alcohol. Consequently, on dissolution of the alkene in an acid, there is no rapid and reversible addition of the proton to the alkene with the subsequent interaction of the ion formed with a water molecule in the rate-limiting step. The exchange for deuterium of the hydrogen atoms attached to the carbon atoms of the double bond was not observed[10–12] in solutions of alkenes and alcohols in acids. Thus the alkene isolated from the reaction mixture after the fiftieth conversion of 2-methylbut-2-ene into an alcohol in 1 M HNO_3 solution in deuteriated water (50% deuterium) did not contain measurable amounts of deuterium.[10] In the alcohol obtained on hydration of isobutene to D_2SO_4, there is only one C–D bond.[11]

This result was subsequently confirmed experimentally[12] in the hydration of isobutene in deuterium-containing perchloric acid. Indeed, if the "classical" carbonium ion is formed and is not in equilibrium with the alkene, then the t-butyl alcohol obtained on hydration of isobutene in the deuteriated acid will contain only one C–D bond:

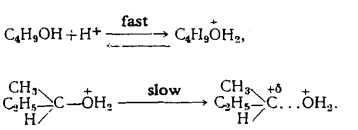


The measurements were performed under conditions where the contribution of the alcohol dehydration reaction to the overall rate of reaction can be neglected. As a rule, the equilibrium hydration of the UC is displaced towards the alcohol and $k_{dehydr} \ll k_{hydr}$. It has also been shown[11] that, on formation of an alkyl sulphate from ethylene, the hydrogen atom does not undergo isotope exchange.

The exchange of a hydrogen atom for deuterium, expected in the presence of Whitmore carbonium ions (σ-complexes), was also not observed in the experiments with arylalkenes. Thus the interaction of 2-phenylpropene has been investigated[13] in ethanol in the presence of a 17% D_2SO_4 solution. After the attainment of 24% and 54% conversions, the deuterium content in the unreacted UC in the five positions of the hydrogen atoms not incorporated in the aromatic ring was only 0 ± 2% in the former case and 10 ± 5% in the latter case. In the same study, it was shown by NMR that, in the formation of the ethyl ether derived from *cis*-2-phenylbut-2-ene (11% D_2SO_4 in C_2H_5OD), the unreacted 2-phenylbut-2-ene contains no hydrogen atoms.

For 15% conversion of styrene-ββ-d_2 to the carbinol in 43.4% $HClO_4$ solution, the unreacted styrene-ββ-d_2 contained no additional D atoms.[13] This fact shows that the exchange of hydrogen atoms cannot precede the rate-limiting step of the hydration reaction and even if a Whitmore carbonium ion is formed it is not in equilibrium with the UC. It is noteworthy that the formation of such carbonium ions is believed to be a thermochemically unfavourable reaction.[14] The results described led investigators to revise the principle postulates of the carbonium ion concept.

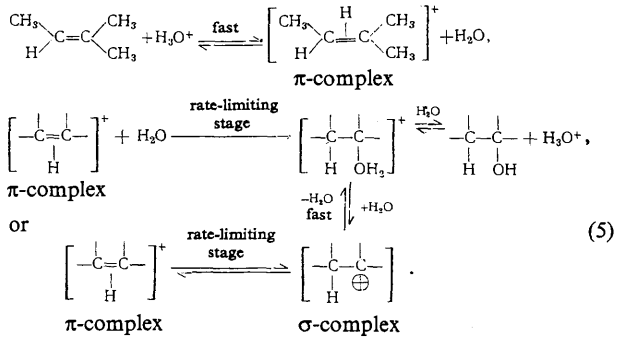
It is believed[15,16] that the intermediate reactive species in the exchange reaction of the oxygen atom in s-butyl alcohol is not a Whitmore carbonium ion but a carbonium ion linked to a water molecule; it is formed from the protonated alcohol in the slow stage and is converted into the product in the rapid stage:



(4)

Such an ion does not exchange the hydrogen atom of the C–H bond for either deuterium or tritium.

It has been suggested[17] that the carbonium ion has the structure of the π-complex proposed by Dewar in which the bond between the proton and the UC is formed via the π-orbitals of the double bond.[18] This proton is not equivalent to the protons attached to the carbon atoms of the double bond. It has been postulated that the π-complex is in equilibrium with the UC and that the concentration of such complexes determines the rate of the limiting step of the hydration of the UC. The proposed equilibrium and rate-limiting steps of the hydration of 2-methylbut-2-ene are described by the equations



(5)

The conclusion that there is an equilibrium between the UC and the π-complex was reached from results of experiments on the hydration of 2-methylbut-2-ene in 0.973 M HNO_3 at 30 °C in a mixture of D_2O and H_2O with different ratios $n = c_{D_2O}/(c_{D_2O} + c_{H_2O})$.[17] An increase in n altered the effective hydration rate constant in the mixed solvent k^n_{hydr}. The observed effect was described quantitatively on the following assumptions: the protonated form of the UC, produced in the equilibrium step, is the reactive form in its hydration; the observed reaction rate is the sum of the rate of hydration via pathways involving the participation of the solvated proton and deuteron; the specific rate constants for these pathways can be measured by employing solutions with $n = 0$ and $n = 1$ respectively; the activity of the protons and deuterons for different n can be calculated from literature data.[19]

It was shown subsequently[12,20] that, in order to describe the dependence of the observed hydration rate constant on n, it is necessary to take into account not only the ratio of the concentrations of protons and deuterons but also the differences between the isotope enrichments of the solvent and the C–H bonds of the alcohol formed on hydration of the UC. According to Scheme (5), the π-complex is obtained from the UC in the rapid and equilibrium stages, while the rate-limiting step of the hydration reaction can be both bimolecular and unimolecular. In the former case, the π-complex reacts with H_2O to produce the protonated form of ROH. In the unimolecular rate-limiting step, the π-complex is converted into a σ-complex, which is subsequently rapidly converted into the protonated alcohol. In the reverse alcohol dehydration reaction, the π-complex should be converted in the rapid and equilibrium step into the σ-complex which is formed according to the mechanisms presented above, on protonation of ROH and then splits off water.

We believe that Scheme (5) can operate only in rare cases, because, in conformity with this Scheme, it has been assumed that the ionisation of ROH and UC reduces solely to the protonation reaction and because the hypothesis of the formation of a π-complex from the UC in the rapid and equilibrium stages is controversial.

As experimental data on the UC hydration and ROH dehydration reactions accumulated, the view according to which the transfer of a proton to the UC in the hydration reaction takes place in the rate-limiting step became increasingly firmly established. Such transfer is indicated by the catalytic acceleration of the hydration reaction by weak acids. For example, the hydration of *p*-methoxy-α-methylstyrene,[21,22] cyanoketen dimethylacetal,[23] and 2-dichloromethylene-1,3-dioxolan[24] is catalysed by carboxylic acids and buffer mixtures. A similar phenomenon has also been observed for other UC.[25,26] It has been suggested that, in catalysis by undissociated molecules of weak acids, the proton is transferred in the rate-limiting step.

The reaction rate constant k and the acid dissociation constant K_{dis} are related by the Brønsted equation

$$k/p = (qK_{dis}/p)^{\alpha},$$

where p and q are statistical corrections and α is a coefficient to which the significance of a measure of the degree of proton transfer in the transition state has been attributed (Ref. 27, p. 345). If $\alpha = 1$, it is assumed that the proton transfer takes place in the equilibrium step. The Brønsted equation has also been used to obtain information about the degree of proton transfer in the rate-limiting step of the hydration of the UC in catalysis by strong acids. For this purpose, measurements were made of the dependence of the rate constant k_{hydr} on n, i.e. on the mole fraction of D_2O in a mixed solvent consisting of D_2O and H_2O or the mole fraction of T_2O and H_2O.[12,23,24] It was found that the dependence of lg k_{hydr} on n for reactions with proton transfer in the equilibrium and rate-limiting steps is described by identical formulae. It is logical to postulate that in the catalysis of the hydration of UC by strong acids in aqueous solutions proton transfer to the UC can also be achieved in the rate-limiting step.

Attempts have also been made on the basis of such ideas to calculate the lifetime of the carbonium ions (carbocations). For example, it has been shown[28] that the lifetime of the carbocations formed from 2,3-dimethylbut-2-ene in dilute aqueous acid solutions ($HClO_4$, H_3PO_4, HSO_4^-) at 25 °C is $\sim 10^{-10}$ s.

The proton transferring agents can be ion pairs, solvated protons, and the molecules of the undissociated acid. This does not naturally rule out the possibility of proton transfer to the UC in the rapid and equilibrium steps.

As already mentioned above, in catalysis by strong acids lg k_{hydr} frequently varies more markedly than H_0. This fact and also the correlation between lg k_{hydr} and the σ^+ constants of the substituents have been explained by proton transfer to the reactant in the rate-limiting step.[13]

In order to test the concept of "classical" carbonium ions, the kinetics of the exchange of ^{16}O for ^{18}O in alcohols have been studied. The results of measurements under identical conditions of the rate constants for such exchange (k_{exch}) and the dehydration of ROH cannot be explained on the assumption that the "classical" carbonium ion is the intermediate reactive species in these reactions. As already mentioned above, it has been suggested[15,16] that the carbonium ion incorporates a water molecule. In the view of the above workers, the exchange of the oxygen atom in the alcohol takes place in the rapid step and the unimolecular step involving the formation of this ion is rate-limiting, as shown in Scheme (4). In the study of the kinetics and mechanism of the exchange of the oxygen atom in alcohols, measurements have been made as a rule also of the rate constant for the dehydration of ROH in order to be certain that the exchange does not occur as a consequence of the reversibility of the ROH dehydration and UC hydration reactions. As a result, a bimolecular mechanism has been proposed for the exchange of the oxygen atom in alcohols.

It has been found[15] that under identical conditions k_{dehydr} for s-butyl alcohol is much smaller than k_{exch}. Subsequent studies demonstrated that this rule holds also in the majority of other cases, but there are exceptions. However, in elucidating the causes of these deviations, additional confirmation of the validity of the bimolecular exchange mechanism was obtained.

Comparison of the rate constants for the exchange involving t-butyl alcohol in ^{18}O-enriched sulphuric acid with the rate of dehydration of the alcohol in the unlabelled acid showed that at 55 °C in 0.045 and 0.45 M H_2SO_4 solutions, the constant k_{exch} is greater than k_{dehydr} by factors of 30 and 27 respectively.[29] At 75 °C in 0.045 M H_2SO_4 solution, $k_{exch}/k_{dehydr} = 20.7$. The alcohol concentration in the experiments was 1.04 M. The constant k_{exch} was greater than k_{dehydr} also in the case of t-pentyl alcohol:[30] at 25 °C, $k_{exch} = 7.72 \times 10^{-4}$ min^{-1} in 0.96 M H_2SO_4 solution, while $k_{dehydr} = 1.59 \times 10^{-4}$ min^{-1} in 1.5 M H_2SO_4 solution. The ROH concentration was 0.5 M in these experiments.

Comparison of the constants k_{exch} and k_{dehydr} for n-butyl and neopentyl alcohols proved to be more complex because the alkenes formed from them at 125 °C in 0.5 M sulphuric acid solution undergo further reactions.[31] The products of the reaction of n-butyl alcohol are s-butyl alcohol, di-n-butyl ether and a mixture of butenes. t-Pentyl alcohol and a mixture of pentenes are formed from neopentyl alcohol. The rate of the decomposition reaction was determined from the decrease in the concentration of the initial alcohol. Table 1 presents the measured[31] k_{exch} and the decomposition rate constants k_{decomp} for n-butyl and neopentyl alcohols.

Table 1. The constants k_{exch} and k_{decomp} for n-butyl (0.729 M) and neopentyl (0.242 M) alcohols at 125 °C (according to the data of Dostrovsky and Klein[31]).

Alcohol	$[H_2SO_4]$, M	$10^2 k_{exch}$, min^{-1}	$10^2 k_{decomp}$, min^{-1}
n-Butyl	0.46	33.6	9.84
Neopentyl	0.48	0.84	30.6

There are good grounds for the assumption that the primary products of the decomposition of n-butyl and t-pentyl alcohols are alkenes whose hydration entails the formation of s- and t-butyl alcohols. One can therefore assume that $k_{decomp} = k_{dehydr}$. According to the data in Table 1, $k_{exch} > k_{dehydr}$ for n-butyl alcohol. On the other hand, $k_{exch} < k_{dehydr}$ for neopentyl alcohol. Thus n-butyl alcohol is more reactive in the exchange reaction than neopentyl alcohol. The experimental data for the exchange of the oxygen atom in ROH[15,29,30] show that the exchange and dehydration proceed via different mechanisms. The same conclusion follows from the results of a study[31] where it was shown that but-1-ene and but-2-ene are formed from n-butyl alcohol in an acid medium, but the product of the hydration of both alkenes is s-butyl alcohol. The formation of the latter from but-1-ene has been demonstrated by experiments on the hydration of [^{14}C]-but-1-ene under conditions similar to those used in the study of the exchange of the ^{16}O atom. s-Butyl and n-butyl alcohols have been obtained from [^{14}C]-but-1-ene, but the content of n-butyl alcohol in the hydration products was only 0.001. Consequently the exchange of ^{16}O in n-butyl alcohol is not a consequence of the dehydration of the latter with subsequent hydration of but-1-ene. It was therefore concluded[31] that the exchange of the oxygen atom in n-butyl alcohol proceeds exclusively via a bimolecular mechanism:

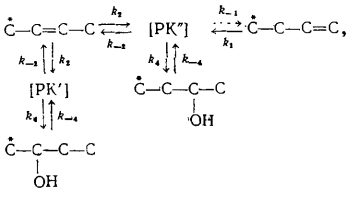
$$H_2{}^{18}O + CH_3(CH_2)_2CH_2OH \rightleftarrows H_2O + CH_3(CH_2)_2{}^{18}OH.$$

It follows from Table 1 that under identical conditions k_{exch} is greater for n-butyl alcohol than for neopentyl alcohol. This can be explained by steric hindrance in the bimolecular exchange mechanism involving neopentyl alcohol.

Fundamental conclusions concerning the mechanisms of the dehydration of ROH, the hydration of UC, and the exchange of the oxygen atom in alcohols have been reached by Manassen and Klein.[32] They investigated the reactions of but-1-ene and s-butyl alcohol in 0.555 M $HClO_4$ solutions at 101.4 °C.

1) $CH_3CH_2CH=CH_2 + H_2O \rightleftarrows CH_3CH_2CH(OH)CH_3$,
2) $CH_3CH_2CH=CH_2 \rightleftarrows CH_3CH=CHCH_3$,
3) $CH_3CH_2CH(OH)CH_3 \rightleftarrows CH_3CH=CHCH_3 + H_2O$,
4) $CH_3CH_2CH(^{18}OH)CH_3 + H_2{}^{16}O \rightleftarrows CH_3CH_2CH(^{16}OH)CH_3 + H_2{}^{18}O$.

Overall, the reactions investigated can be represented by the following Scheme:



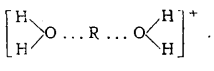
where [PK′] and [PK″] are reactive complexes.

Analysis showed that

$$k_{isom} = k_{-1}k_2/(k_2 + k_4),$$

where k_{isom} is the isomerisation rate constant.

Using 2-butanol labelled with ^{18}O and ^{14}C, it was possible to investigate under the same conditions the exchange of the oxygen atom of the alcohol with water and the isomerisation of the alcohol. It was found that $k_{isom} = (3.102 \pm 0.072) \times 10^{-4}$ min^{-1} and $k_{exch} = (4.490 \pm 0.093) \times 10^{-4}$ min^{-1}. The authors[32] believe that the data for all four reactions investigated can be best described by assuming that the intermediate is a planar carbonium ion linked to a water molecule on either side of the plane; the central carbon atom is thus "pentavalent". The intermediate in the reaction involving the exchange of the oxygen atom in ROH has in their view the composition



This composition of the intermediate was also adopted in subsequent studies (see, for example, McClellend[33]).

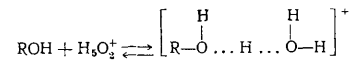
The ideas about the equilibrium and rate-limiting steps in the dehydration of ROH, the hydration of UC, and the exchange of the oxygen atom in alcohols described above do not permit a quantitative description of the effect of the ionising capacity of the aqueous acid solution on the experimental (effective) rate constants for these reactions. This situation can be accounted for by the fact that, in the analysis of kinetic data obtained in solutions at a variable concentration of the acid catalyst, no account is taken of the fact that (1) the protonated form of the reactant B is the complex BH_3O^+ [see Eqn. (1)], (2) the intermediates are not only such ions but also complexes of the reactant-base with acid molecules, acid hydrates, etc., and (3) when the concentration of the acid in solution is varied within wide limits the hydration and dehydration reactions can proceed via several pathways, i.e. all the ions and molecules capable of forming a reactive complex with the reactants can exhibit a reactivity. The relative contribution of each pathway to the effective rate constant depends on the acid concentration.

An attempt is made below to explain certain literature data taking into acocunt the mechanism proposed for the ionisation of acids.

III. A method for the determination of the mechanism of the dehydration of alcohols and the hydration of unsaturated compounds from kinetic data

The modern physical methods do not permit the determination of the concentration and composition of the intermediate reactive complexes RC in the course of a kinetic experiment on the hydration of UC and the dehydration of ROH. Conclusions concerning the composition of RC and the influence of the medium on their concentration have been made on the basis of the dependence of k_{hydr} and k_{dehydr} on the ionising properties of the medium. The mechanism of the ionisation of alcohols in acid media has not so far been studied in detail and there are no reliable data for the basicity constants of aliphatic alcohols. However, there is no doubt that the ionisation of alcohols can lead to the formation of protonated forms, ion pairs, and complexes with components of the solution (for example, with the acid molecules HA).

According to Vinnik et al.,[5] the formation reaction of the protonated form of the alcohol ($ROH.H_3O^+$) can be described by the equation



The hypothesis of the formation of the ion pair $ROH.H_3O^+.A^-$ and the complexes ROH.HA has been justified by experimental data for the ionisation of tertiary amines, azulene and its derivatives,[3] and also indole derivatives[34] in moderately concentrated and concentrated aqueous solutions of strong acids. It follows from the literature data described above that hitherto there have been no clear-cut ideas about the structure and properties of the ionised form of the alkene in aqueous acid solutions. The function which would make it possible to take into account the influence of the acidity of the medium on the degree of conversion of the UC into the ionised form is also unknown. The ionised form can be produced either in the equilibrium or in the rate-limiting states. Unfortunately, most investigators assume that in aqueous solutions of strong acids the ionisation of bases reduces solely to their protonation and in cases where it is not possible to describe the experimental data they assume that the ratio of the activity coefficients of the unionised and protonated forms of the test base and of the Hammett indicators depends on the acid concentration in different ways.

There have also been attempts to select correlation equations for the description of such reactions. It has been suggested that the ionisation of each base is described by its own acidity function.[35–37] For example, we may designate such a function for the UC by H_s. The function H_0 measured by means of indicators and the function H_s are linked by the equation

$$H_s + \lg c_{H^+} = (1 - \Phi_c)[H_0 + \lg c_{H^+}], \quad (6)$$

which has been obtained on the assumption that

$$\lg f_{H^+} - \lg \frac{f_{SH^+}}{f_S} = (1 - \Phi_c)\left[\lg f_{H^+} - \lg \frac{f_{BH^+}}{f_B}\right],$$

where f are the concentration activity coefficients of the corresponding species, c_{H^+} is the concentration of solvated protons, and Φ_c is a coefficient independent of the H_0 for the medium according to its significance.

If the reactive species is a protonated form of the UC produced in the equilibrium stage and converted into the reaction products in the

rate-limiting stages, then, provided that the degree of protonation of the UC is low, we obtain according to Lucchini et al.[35]

$$\lg k_{hydr} + H_0 = \lg k_0 + (\Phi_{RC} - \Phi_c)[H_0 + \lg c_{H^+}],$$

where k_0 is a constant and Φ_{RC} is a coefficient corresponding to Φ_c when the base is RC.

On the other hand, if the proton adds to the UC in the slow stage, i.e.

$$UC + H_5O_2^+ \xrightarrow{slow} RC \rightarrow \text{products},$$

then

$$\lg k_{hydr} + H_0 = \lg k_0 + \Phi_{RC}[H_0 + \lg c_{H^+}].$$

When this method of analysis of kinetic data is used, one cannot naturally obtain information about the specific reaction mechanism, the composition of the RC, and about the equilibrium and rate-limiting stages.

If the rate-limiting stage is the formation of the protonated form, then it is believed[38,39] that the rate of protonation of bases can be characterised by means of the kinetic activity function H_c^*. An attempt has been made to apply this function in the analysis of data for the kinetics of the hydration of styrene and its derivatives.[40]

It is important to note that the attempts to explain the kinetics of the UC hydration and ROH dehydration reactions solely on the basis of the concept of carbonium ions as intermediate reactive species simplified the real mechanism of these reactions because no account was then taken of the catalytic action of other ions, neutral species, and ion pairs in the aqueous solution of strong acids.

As can be seen from Eqn. (2), k_{hydr} and k_{dehydr} are effective overall constants. In order to elucidate their physical significance, it is essential to establish how they depend on the ionising capacity of the acid solutions a_δ. The ionisation reaction of UC and alcohols can be described with the aid of the equations

$$UC + \delta \overset{K_i^{UC}}{\rightleftarrows} UC.\delta,$$

$$ROH + \delta \overset{K_i^{ROH}}{\rightleftarrows} ROH \cdot \delta,$$

where K_i^{UC} and K_i^{ROH} are the ionisation equilibrium constants. Ions or molecules whose addition converts the reactant into the ionised form are designated by

$$K_i^{UC} = \frac{a_{UC}a_S}{a_{UC.\delta}} = \frac{c_{UC}}{c_{UC.\delta}} a_\delta \frac{f_{UC}}{f_{UC.\delta}},$$

$$K_i^{ROH} = \frac{a_{ROH}a_\delta}{a_{ROH\cdot\delta}} = \frac{c_{ROH}}{c_{ROH\cdot\delta}} a_\delta \frac{f_{RCH}}{f_{ROH\cdot\delta}}.$$

In many reactions in acid solutions, the intermediate RC is either the ionised form of the reactant or its complex with the molecules and ions from the solution. Equations designed to take into account the influence of the medium on the rates w and the hydration and dehydration rate constants, derived on the assumption that the catalytic action of the acid is due to the conversion of the reactant into the ionised form, which is either itself the RC or is capable of forming such RC rapidly and reversibly on interaction with species from the solution, are presented below. If the RC in the dehydration reaction has the composition ROH.δ, then

$$w_{dehydr} = k\frac{a^*}{f^*} = k\frac{a_{RC}}{f^*} = \frac{k_{true}}{K_i^{ROH}}\frac{a_{ROH}a_\delta}{f^*} = \frac{k_{true}}{K_i^{ROH}} c_{ROH}a_\delta \frac{f_{ROH}}{f^*},$$

$$\frac{w_{dehydr}}{c_{ROH}} = \frac{k_{true}}{K_i^{ROH}} a_\delta \frac{f_{ROH}}{f^*} = k_{dehydr}, \qquad (7)$$

where k_{true} is the true rate constant independent of the acid concentration in the aqueous solution, a^* and f^* are respectively the activity and the activity coefficient of the activated complex, and a_{RC} is the activity of the RC expressed in terms of the activity of the unionised alcohol ROH and the species δ.

Since the UC hydration and ROH dehydration reactions proceed via the same RC, in its formation from the UC a water molecule should add to the ionised form UC.δ:

$$UC.\delta + H_2O \overset{K_{RC}^{UC}}{\rightleftarrows} RC,$$

$$K_{RC}^{UC} = a_{UC.\delta}\, a_{H_2O}/a_{RC}. \qquad (8)$$

Then

$$w_{hydr} = k\frac{a^*}{f^*} = k\frac{a_{RC}}{f^*} = \frac{k_{true}}{K_{RC}^{UC}}\frac{a_{UC.\delta}a_{H_2O}}{f^*} =$$

$$= \frac{k_{true}}{K_{RC}^{UC}}\frac{a_{UC}a_\delta a_{H_2O}}{K_i^{UC}f^*} = \frac{k_{true}c_{UC}a_{H_2O}f_{UC}a_\delta}{K_{RC}^{UC}K_i^{UC}f^*}, \qquad (9)$$

$$\frac{w_{hydr}}{c_{UC}} = \frac{k_{true}}{K_{RC}^{UC}K_i^{UC}} a_{H_2O}a_\delta \frac{f_{UC}}{f^*} = k_{hydr}.$$

In Eqns. (7) and (9), w_{dehydr} and w_{hydr} are the rates of dehydration of ROH and hydration of UC in an aqueous solution with a specified acid concentration. These equations were obtained subject to the condition that the degree of conversion of ROH and UC into the ionised form is low. In Eqns. (7) and (9), δ denotes the following species:

(1) the H_3O^+ ions participating in the protonation of the base, whereupon $a_\delta = h_0$,

(2) the $H_5O_2^+$ ions participating in the formation of the RC in accordance with the equation

$$ROH + H_5O_2^+ \rightleftarrows ROH\cdot H_5O_2^+; \qquad (10)$$

whereupon $a_\delta = a_{H_5O_2^+} = h_0 a_{H_2O}$, since one can assume that $h_0 = a_{H_3O^+}$,[5]

(3) the ion pairs $H_3O^+.A^-$ participating in the formation of the complex in accordance with the equation

$$ROH + H_3C^+\cdot A^- \rightleftarrows ROH\cdot H_3O^+\cdot A^-; \qquad (11)$$

whereupon $a_\delta = a_{HA}.a_{H_2O}$, i.e. the activity of the ion pair of the strong acid $H_3O^+.A^-$ is expressed in terms of the product of the thermodynamic activities of the acid (a_{HA}) and water (a_{H_2O}), and

(4) the acid molecules HA participating in the formation of the complex of the base with one or two molecules of the undissociated acid:

$$ROH + HA \rightleftarrows ROH\cdot HA, \qquad (12)$$

$$ROH + 2HA \rightleftarrows ROH\cdot 2HA; \qquad (13)$$

in the first case $a_\delta = a_{HA}$ and in the second $a_\delta = a_{HA}^2$.

Naturally, these examples do not exhaust the possibilities for the complex formation (ionisation) of bases in aqueous solutions of strong acids.

Eqns. (7) and (9) can be used to find the composition of the RC from kinetic data. For this purpose, it is essential to establish the dependence of k_{dehydr} on known functions characterising the ionising capacity of the acid solution. The problem reduces to the selection of a function a_δ for the description of the influence of the medium on the effective rate constant subject to the conditions that the multipliers f_{ROH}/f^* and f_{UC}/f^+ in Eqns. (7) and (9) respectively are independent of the acid concentration in solution.[41]

Unfortunately, it has not so far been established unambiguously how the ratios $f_{ROH}/f_{ROH.\delta}$ and $f_{UC}/f_{UC.\delta}$ really change when the acid concentration in solution is varied. In many cases, the reactive form of alcohols is the protonated form, its complexes with water molecules, and ion pairs, and the influence of the medium on the effective rate constant can frequently be described by assuming that $f_{ROH}/f_{ROH.\delta}$ is independent of the acid concentration in solution. This can be explained by the fact that, as in the ionisation of nitroanilines, in the ionisation of alcohols the rearrangement of the electronic structure of the molecule has little effect on its solvating capacity.

The formation of the arenium carbonium ion is accompanied by a significant rearrangement of the electronic structure of the UC.[42,43] Although the structures of the ionised form of aliphatic UC have not so far been established, there are grounds for the assumption that in the given instance the electronic structure of the UC rearranges. Hence it follows that, depending on the medium, there is a possibility that in the ionisation of the UC the ratios of the activity coefficient of the unionised and ionised forms of the UC may change.

It is known that, when the acid concentration in aqueous solution is varied, the activity coefficients of the unionised forms of the UC (f_{UC}) and of the alcohol obtained from it (f_{ROH}) do not vary in the same way. Consequently, depending on the composition of the medium, the quantities $f_{ROH}/f_{ROH.\delta}$ and f_{UC}/f^* should also vary in different ways.

The reactive complex ROH.δ is one of the ionised forms of the alcohol; Eqns. (10)–(13) reflect the stoichiometry of their formation. Taking into account the arguments described above stating that the composition of the medium does not influence the ratio $f_{ROH}/f_{ROH.\delta}$, one may postulate that in the ROH dehydration reaction it is also independent of the acid concentration. The reactions analysed in this review are slow and we therefore assume that the reactive complex and the activated complex obtained from it are in equilibrium with the reactants. This enables us to assume that the ratios f_{ROH}/f^* and f_{ROH}/f_{RC}^{ROH} vary in the same way as the acidity of the medium is varied (the activity coefficient of RC in the ROH dehydration and UC hydration reactions is designed by f_{RC}^{ROH}).

We replaced f^* in Eqn. (2) by f_{ROH}/f_{RC}^{ROH}, whereupon

$$k_{dehydr} = \frac{k_{true}}{K_i^{ROH}} a_\delta \frac{f_{ROH}}{f_{RC}^{ROH}}. \quad (14)$$

By adjusting f_{ROH} and f_{RC}^{ROH} to water as the standard and by setting them equal to unity, we obtain

$$k_{dehydr} = \frac{k_{true}}{K_i^{ROH}} a_\delta. \quad (15)$$

Eqn. (14) can be used to establish the composition of the RC from kinetic data.

In order to determine the composition of the activated complex in the ROH dehydration reaction, it is necessary to select a species δ such that Eqn. (7) for k_{dehydr} includes the multiplier f_{ROH}/f^*, which is independent of the acid concentration in solution. The function a_δ found in this way does in fact characterise the composition of the RC. For this purpose, it is essential to know the rate constant for the hydration of the UC and for the dehydration of the ROH obtained from it under identical conditions.

Unfortunately, despite the comparatively large number of studies on the hydration of UC and the dehydration of ROH, the equilibrium concentrations of the UC and the ROH and hence the constants k_{dehydr} and k_{hydr} found under identical conditions are quoted in only an insignificant proportion of the relevant communications.

The available data (which are admittedly very few in number) confirm the above postulate: the multiplier f_{ROH}/f_{RC}^{ROH} in Eqn. (14), reflecting the influence of the medium on k_{dehydr}, does not change within the limits of the error of the measurement as the acid concentration in aqueous solution is varied. This is illustrated by the data in Tables 2–4, which present the constants k_{hydr} and k_{dehydr}, the function a_δ, and the ratios k_{dehydr}/a_δ and $k_{hydr}/a_\delta a_{H_2O}$ for the hydration and dehydration reactions.

Judging from the data in Table 2, a virtually constant ratio $k_{dehydr}/h_0 a_{H_2O}$ is retained during the dehydration of 2-cyclohexenol in the H_2SO_4 concentration range 4.9–42.0%. The function a_δ is in this case equal to $h_0 a_{H_2O}$ and the RC and the activated complex are therefore formed via the addition of the $H_5O_2^+$ ion to the ROH molecule and in the case of UC via the addition of the $H_5O_2^+$ ion and the H_2O molecule. The ratio $c_{ROH}^\infty/c_{UC}^\infty = f_{UC}/f_{ROH}$ depends significantly on the acid concentration in solution. Consequently the function $a_\delta a_{H_2O} = h_0 a_{H_2O}^2$ does not describe the influence of the medium on the ionisation of cyclohexa-1,3-diene.

Table 2. Kinetics of the hydration of cyclohexa-1,3-diene and the dehydration of 2-cyclohexenol (according to the data of Jensen et al.[44]).

$[H_2SO_4]$, wt.%	$10^2 k_{dehydr}$, min^{-1}	$10^2 k_{hydr}$, min^{-1}	$lg(k_{dehydr}/h_0 a_{H_2O})$	$lg(k_{hydr}/h_0 a_{H_2O})$	$c_{ROH}^\infty/c_{UC}^\infty$
Temperature 70 °C					
4.9	1.7	3.3	−1.60	−1.30	1.92
9.7	4.1	10.9	−1.64	−1.19	2.65
21.7	17.3	76.9	−1.73	−1.01	4.45
32.2	61.7	345.0	−1.74	−0.88	8.72
Temperature 60 °C					
4.9	0.5	0.9	−2.13	−1.95	1.90*
9.7	1.5	3.7	−2.07	−1.67	2.46
21.7	6.8	29.0	−2.16	−1.47	4.24
32.2	22.4	125.0	−2.25	−1.37	5.59
Temperature 40 °C					
21.7	0.95	4.0	−3.09	−2.40	4.23
32.2	4.15	25.2	−3.09	−2.16	6.31
42.0	15.6	199.8	−3.07	−1.67	12.8

*The equilibrium UC and ROH concentrations are not quoted by Jensen et al.[44] They were calculated using the values of $c_{ROH}^\infty/c_{UC}^\infty$ at 70 and 80 ° C.

Similar conclusions follow from the results obtained in the study of the hydration of 2-phenylpropene and the dehydration of 2-phenyl-2-propanol in H_2SO_4 solutions[13] (Table 3) and of the dehydration of t-pentyl alcohol in HNO_3 solutions[30] (Table 4).

The virtual constancy of the quantity $k_{dehydr}/h_0 a_{H_2O}$ when the composition of the medium is varied implies that the activity of the RC in these reactions should be expressed in terms of the product of the activities of ROH and the $H_5O_2^+$ ion for the dehydration of ROH and in terms of the activities of the $H_5O_2^+$ ion and the water molecule in the hydration reaction.

There are instances where k_{hydr} and k_{dehydr} vary in the same way as the acid concentration is varied. Evidently, in the determination of the reaction mechanism from the influence of the composition of

the medium on k_{hydr} in such cases one must take into account the fact that, in the formation of the RC, one H_2O molecule more adds to the UC than to the ROH.

Table 3. Kinetics of the hydration of 2-phenylpropene and the dehydration of 2-phenyl-2-propanol at 25 °C (according to the data of Deno et al.;[13] k_{hydr} and k_{dehydr} are expressed in min^{-1}).

$[H_2SO_4]$, wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$\lg \frac{k_{hydr}}{h_0 a_{H_2O}}$	$\lg \frac{k_{dehydr}}{h_0}$	$\lg \frac{k_{hydr}}{h_0 a_{H_2O}^2}$	$\lg \frac{k_{dehydr}}{h_0 a_{H_2O}}$
4.8	−1.99	−3.14	−1.87	−3.03	−1.86	−3.02
9.8	−1.59	−2.62	−1.90	−2.95	−1.88	−2.93
19.6	−0.82	−2.02	−1.80	−3.05	−1.75	−3.00
29.6	−0.12	−1.27	−1.70	−2.97	−1.58	−2.85
40.5	+0.72	−1.05	−1.50	−3.52	−1.25	−3.27

Table 4. Kinetics of the dehydration of t-pentyl alcohol in nitric acid at 30 °C [the values of k_{dehydr} (in min^{-1}) were taken from Boyd et al.[30]].

$[HNO_3]$, M	$-\lg k_{dehydr}$	$-H_0$	$-\lg a_{H_2O}$	$-\lg(k_{dehydr}/h_0 a_{H_2O})$
0.973	3.86	0.29	0.02	4.13
1.50	3.51	0.58	0.03	4.06
2.01	3.29	0.79	0.03	4.05
3.00	2.91	1.12	0.05	3.98
4.00	2.70	1.45	0.07	4.07
4.94	2.51	1.68	0.10	4.09

Table 5. Kinetics of the hydration of 2-(4-methoxyphenyl)propene and the dehydration of 2-(4-methoxyphenyl)-2-propanol in sulphuric acid at 25 °C [the values of k_{hydr} (min^{-1}) and k_{dehydr} (min^{-1}) were taken from Deno et al.[13]].

$[H_2SO_4]$, wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$\lg(k_{hydr}/h_0)$	$\lg(k_{dehydr}/h_0)$	$\lg(k_{dehydr}/a_{H_2SO_4})$	$\lg(k_{dehydr}/a_{H_2SO_4}a_{H_2O})$	$c^{\infty}_{ROH}/c^{\infty}_{UC}$
4.8	−0.37	−1.44	−0.28	−1.33	2.32	1.25	11.7
7.1	−0.18	−0.99	−0.30	−1.11	2.12	1.31	6.8
9.8	−0.13	−0.66	−0.20	−0.99	2.08	1.29	6.7
14.1	+0.46	−0.14	−0.20	−0.80	1.93	1.33	3.7

Table 5 presents data for the hydration of 2-(4-methoxyphenyl)-propene and the dehydration of the corresponding alcohol in aqueous H_2SO_4 solutions, from which it follows that, when the acid concentration is varied from 4.8 to 14.1 wt.%, $c^{\infty}_{ROH}/c^{\infty}_{UC}$ and hence f_{ROH}/f_{UC} vary by a factor of 3.17. The ratios $k_{dehydr}/a_{H_2SO_4}a_{H_2O}$ and k_{hydr}/h_0 hardly vary with composition.

From the above, one must assume that in the given instance the constancy of the quantity $k_{dehydr}/a_{H_2SO_4}a_{H_2O}$ indicates the formation of an RC from the ROH, an H_2SO_4 molecule, and an H_2O molecule. The constancy of k_{hydr}/h_0 does not characterise the mechanism of the rate-limiting step.

From the results presented, we assume that, when the strong acid concentration in aqueous solution is varied, the ratio f_{ROH}/f^{ROH}_{RC} hardly changes.

Thus, in order to establish the mechanism of the rate-limiting step of the hydration of the UC and of the dehydration of the ROH, it is necessary to find by Eqn. (15) the function a_δ in order to determine the influence of the acid concentration in solution on k_{dehydr}. The function a_δ is the activity of the species or complex which adds to the reactant and converts it into the RC. The latter is in equilibrium with the activated complex and with the molecules and ions from which it is formed. There is also a possibility of reactions where the RC is not formed. In such cases, a_δ is a function describing the influence of the medium on the activity of the activated complex and the term ka_{RC}/f^* should be eliminated from Eqns. (7) and (9).

Thus the determination of the mechanism of the UC hydration and ROH dehydration reactions reduces to finding the function a_δ from data for the dependence of k_{dehydr} on the ionising properties of the medium. We suggest that such information about the dependence of k_{hydr} on the ionising properties of the medium cannot be obtained without taking into account the contribution by the multiplier f_{UC}/f^* [see Eqn. (16)] to k_{hydr}. For this purpose, it is essential to measure the equilibrium concentrations c^{∞}_{ROH} and c^{∞}_{UC} in experiments on the hydration of the UC.

Since the ratio f_{ROH}/f^* does not change as the acid concentration in solution is varied, f^* in Eqn. (9) can be replaced by f_{ROH}, whereupon

$$k_{hydr} = \frac{k_{true}}{K^{UC}_{RC} K^{UC}_{i}} a_{H_2O} a_\delta \frac{f_{UC}}{f_{ROH}}. \qquad (16)$$

The ratio f_{UC}/f_{ROH} can be found knowing the equilibrium constant K_{eq} for the UC hydration reaction:

$$K_{eq} = \frac{c^{\infty}_{ROH}}{c^{\infty}_{UC} a_{H_2O}} \frac{f_{ROH}}{f_{UC}}. \qquad (17)$$

Simultaneous solution of Eqns. (16) and (17) yields the formula for the determination of a_δ using k_{hydr}:

$$k_{hydr} = \frac{k_{true}}{K^{UC}_{RC} K^{UC}_{i} K_{eq}} a_\delta \frac{c^{\infty}_{ROH}}{c^{\infty}_{UC}}. \qquad (18)$$

There are cases where the ratio $c^{\infty}_{ROH}/c^{\infty}_{UC}$ is independent of the acid concentration in the aqueous solution and k_{dehydr} and k_{hydr} vary in the same way as the ionising properties of the medium are varied.[22,45,46] The function a_δ found with the aid of Eqns. (16) and (18) yields in this case information about the species which reacts with ROH rapidly and reversibly to form the RC. For the formation of such a complex from the UC, the particiption of a water molecule is also necessary. Examples illustrating the wide variety of the mechanisms of the dehydration of ROH and the hydration of the UC are presented below. It follows from the data in Table 2 that the RC in the 2-cyclohexenol dehydration reaction and cyclohexa-1,3-diene hydration reaction is formed from an ROH molecule and the $H_5O_2^+$ ion in conformity with Eqn. (10). In the rate-limiting stage, this complex decomposes to the reaction products

(UC, H_2O, ROH) and the catalyst $H_5O_2^+$ is regenerated simultaneously:

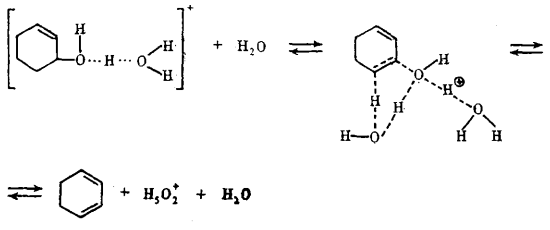
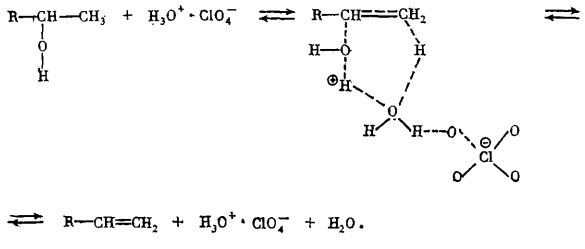


Table 6. Kinetics of the dehydration of 1-phenylethanol and the hydration of styrene in perchloric acid at 25 °C [the values of k_{hydr} (min^{-1}) and k_{dehydr} (min^{-1}) were taken from Schubert and Keefe[22]].

[$HClO_4$], wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$\lg(k_{dehydr}/a_{HClO_4}a_{H_2O})$
36.40	−2.48	−4.11	−6.67
39.50	−2.13	−3.76	−6.69
43.40	−1.62	−3.23	−6.68
47.10	−1.04	−2.65	−6.67
49.25	−0.69	−2.30	−6.65
51.90	−0.30	−1.87	−6.67

In the hydration reaction of styrene and its derivatives and in the dehydration reactions of the corresponding alcohol in perchloric acid, the $H_3O^+.ClO_4^-$ ion pairs are catalytically active (Table 6).[22] In this reaction, the RC are formed from ROH and an ion pair of the type $H_3O^+.A^-$, where A^- is the ClO_4^- anion [see Eqn. (11)]:



The sums $k_{dehydr} + k_{hydr}$ and the ratios $c^{\infty}_{ROH}/c^{\infty}_{UC}$ have been obtained in experiments at 25 °C in perchloric acid not only with styrene (36.4−51.9% $HClO_4$) but also with *p*-ethylstyrene (29.5−41.9% $HClO_4$), *p*-chlorostyrene (36.45−51.9% $HClO_4$), *p*-methoxy-α-methylstyrene (1.03−29.5% $HClO_4$), and *p*-nitrostyrene (59.0−68.5% $HClO_4$).[22] The reactions of the reactants enumerated, except the last two, proceed only via the mechanism with $a_\delta = a_{HClO_4}a_{H_2O}$. In this case, the quantities

$$\lg(k_{dehydr}/a_{HClO_4}a_{H_2O}) = \lg(k_{true}/K_i^{ROH})_{HA.H_2O}$$

are −7.11 ± 0.003, −6.67 ± 0.04, and −5.49 ± 0.08 for *p*-chlorostyrene, styrene, and *p*-methylstyrene respectively. The same mechanism operates in the reaction of *p*-methoxy-α-methylstyrene in solutions at $HClO_4$ concentrations of 20.65% and above, where $\lg(k_{true}/K_i^{ROH}) = -3.82 \pm 0.03$. In more dilute $HClO_4$ solutions, the reaction also proceeds via the mechanism with $a_\delta = h_0 a_{H_2O}$. Schubert and Keefe[22] quote $c^{\infty}_{ROH}/c^{\infty}_{Cu}$ for *p*-nitrostyrene only in the experiment with 63% $HClO_4$ solution. We assumed that, as for the other reactants listed above, this quantity is independent of the $HClO_4$ concentration. The ratio $k_{dehydr}/a_{HClO_4}a_{H_2O}$ for *p*-nitrostyrene is not constant. We explain this by the fact that the dehydration of 1-(*p*-nitrophenyl)-ethanol and the hydration of *p*-nitrostyrene proceeds via two pathways and that their contributions to k_{dehydr} and k_{hydr} are comparable in the test solutions. For one pathway, $a_\delta = a_{HClO_4}a_{H_2O}$ at 25 °C and $\lg(k_{true}/K_i^{ROH})_{HA} = -9.96$ while for the other pathway $a_\delta = a_{HA}$ and $\lg(k_{true}/K_i^{ROH})_{HA} = -10.89$ (in the given case HA is $HClO_4$).

This mechanism of the catalytic action of aqueous acid solutions operates, as will be shown below, also in reactions with other reactants. The constancy of the ratio $k_{dehydr}/a_{HClO_4}a_{H_2O}$ is evidence that the catalytic action is manifested in this reaction by ion pairs with participation of the acid. The effect of the anion reduces in our view to the facilitating the abstraction of the H atom from a C−H bond in the ROH and in transferring it to a carbon atom in the UC. It follows from the data in Table 5 that, in the dehydration of 2-(4-methoxyphenyl)-2-propanol in sulphuric acid, the ratio $k_{dehydr}/a_{H_2SO_4}$ also remains constant. Unfortunately experiments were performed in dilute sulphuric acid solutions where the activity of water changes little. Therefore in the present instance there is no certainty that the function a_δ is equal to the activity of sulphuric acid $a_{H_2SO_4}$ and not to the activity of the $H_3O^+.HSO_4^-$ ion pairs.

The catalytic action of sulphuric acid molecules can be illustrated by data for the dehydration of β-hydroxy-β-phenylpropionic acid (Table 7).[47] The quantity $k_{dehydr}a_{H_2SO_4}$ in 38.32% H_2SO_4 solution is greater than its average value for the range 39.68−69.0% H_2SO_4. This can be explained by the contribution of yet another dehydration pathway which is manifested in more dilute solutions. The numerical values of $\lg(k_{true}/K_i^{ROH})_{HA}$ are −5.78 ± 0.01 at 45 °C and −6.50 ± 0.11 at 25 °C.

The values of k_{dehydr} for β-(*p*-chlorophenyl)-β-hydroxypropionic acid in 53.46−64.13% sulphuric acid solutions at 45 °C have been published.[48] In these solutions, $a_\delta = a_{H_2SO_4}$ and $\lg(k_{true}/K_i^{ROH})_{HA} = -5.25 \pm 0.1$. It follows from Eqn. (12) that the reaction complex with $a_\delta = a_{HA}$ is formed from ROH and an acid molecule (in our case H_2SO_4):

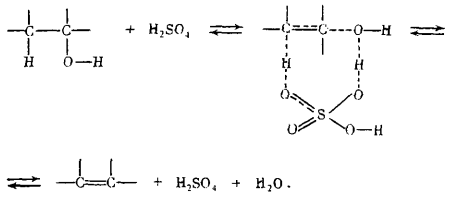


Table 7. Kinetics of the dehydration of β-hydroxy-β-phenylpropionic acid in sulphuric acid at 44.7 °C [the values of k_{dehydr} (min^{-1}) were taken from Noyce and Lane[47]].

[H_2SO_4], wt.%	$\lg k_{dehydr}$	$\lg a_{H_2SO_4}$	$\lg(k_{dehydr}/a_{H_2SO_4})$
38.32	−3.69	−0.89	−4.58
39.68	−3.62	+1.06	−4.68
51.87	−2.19	+2.53	−4.72
58.05	−1.36	+3.40	−4.76
65.45	−0.36	+4.51	−4.87
65.45	−0.32	+4.51	−4.83
69.00	+0.25	+5.03	−4.78
69.00	+0.26	+5.03	−4.77

ROH dehydration and UC hydration reactions are also known in which the catalytic action of the acid is caused by the formation of a complex from the ROH and two acid molecules, i.e. $a_\delta = a_{HA}^2$—for example, the dehydration reactions of the alcohols $XC_6H_4CH.(CF_3)CH_2OH$ and the hydration reactions of the alkenes $XC_6H_4C.(CF_3)=CH_2$ (X = *p*-Me, H, or *p*-Cl) in concentrated sulphuric acid at 25 °C. Calculation based on literature data[49] shows that the quantities $\lg(k_{dehydr}/a^2_{H_2SO_4}) = \lg(k_{true}/K_i^{ROH})_{HA^2}$ are respectively -18.51 ± 0.11 (X = H), -18.86 ± 0.05 (X = *p*-Me, in the range 76.3–83.6% H_2SO_4), and -18.95 ± 0.08 (X = *p*-Cl, in the range 83.6–87.1% H_2SO_4). Judging from the above data,[49] for X = *p*-MeO the reaction at H_2SO_4 concentrations in the range 70.1–76.1% proceeds mainly via the formation of an RC with $a_\delta = a_{H_2SO_4}$; under these conditions, $\lg(k_{dehydr}/a_{H_2SO_4}) = \lg(k_{true}/K_i^{ROH})_{HA} = -10.3$.

Thus it follows from the data in Tables 2–8 that the catalysis of the ROH dehydration and UC hydration reactions in aqueous solutions of acids is determined by the formation of complexes of the reactants with $H_5O_2^+$ ions, $H_3O^+.A^-$ ion pairs, and HA acid molecules. These examples illustrate the catalytic activity of species of predominantly one type among those listed above. However, when the range of acid concentrations is extended and also when the temperature is varied, other reaction pathways also operate. This is seen, in particular, from the data in Table 7.[47] At relatively low sulphuric acid concentrations, the quantity $k_{dehydr}/a_{H_2SO_4}$ for the dehydration reaction of β-hydroxy-β-phenylpropionic acid is greater than in more concentrated solutions, which can be explained by the contribution of yet another reaction pathway. As noted above, the influence of the medium on k_{dehydr} for 1-*p*-nitrophenylethanol and k_{hydr} for *p*-nitrostyrene[22] may be caused by the operation of two pathways: via the formation of an RC with $a_\delta = a_{H_2SO_4}$ and an RC with $a_\delta = a_{H_2SO_4}a_{H_2O}$. the latter variant was first examined by Osipova et al.[50] In this case, the following equation should hold:

$$k_{dehydr} = k_{dehydr}^{HA.H_2O} a_{H_2SO_4} a_{H_2O} + k_{dehydr}^{HA} a_{H_2SO_4}.$$

Table 8. Kinetics of the hydration of $C_6H_5C(CF_3)=CH_2$ and the dehydration of the corresponding alcohol [the values of k_{dehydr} (min^{-1}) and k_{hydr} (min^{-1}) were taken from Koshy et al.[49]].

$[H_2SO_4]$, wt.%	$\lg k_{dehydr}$	$\lg k_{hydr}$	$\lg(k_{dehydr}/a^2_{H_2SO_4})$
87.1	−1.27	−1.83	−18.53
87.1	−1.23	−1.79	−18.48
84.9	−1.92	−2.28	−18.62
83.6	−2.14	−2.43	−18.43
80.9	−2.94	−3.01	−18.48
79.9	−3.30	−3.28	−18.52

The dehydration of β-hydroxy-β-(*p*-methoxyphenyl)propionic acid also proceeds via two pathways. This follows from data in a communication[48] in which the values of k_{dehydr} at 45 °C for 1.0–24.85% H_2SO_4 solutions and at 25 °C for 24.18–47% H_2SO_4 solutions are presented. In experiments with relatively low acid concentrations, it was seen that, with increase in the H_2SO_4 concentration, the main reaction pathway becomes the second one. Table 9 shows that, in the H_2SO_4 concentration range 1.0–18.7%, the quantity $k_{dehydr}/h_0a_{H_2O}$ is practically constant. This permits the assumption that in such solutions the reaction proceeds via only one pathway—via the formation of an RC with $a_\delta = h_0a_{H_2O}$ and that

$$\lg(k_{dehydr}/h_0\,a_{H_2O}) = \lg(k_{true}/K_i^{ROH})_{H_2O_2^+} = -1.60 \pm 0.08.$$

In more concentrated solutions, the quantity $\lg(k_{dehydr}/h_0a_{H_2O})$ increases but the data are insufficient for a quantitative estimation of the contribution by the second pathway. At 25 °C the experiments were performed in more concentrated solutions, which made it possible to calculate the rate constants for the first and second pathways with the aid of the equation

$$k_{dehydr} = k_{dehydr}^{H_5O_2^+} h_0 a_{H_2O} + k_{dehydr}^{HA} a_{H_2SO_4}.$$

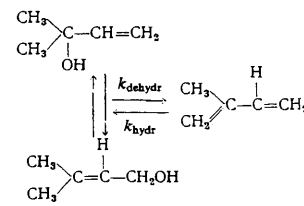
Thus at 25 °C we have

$$\lg(k_{true}/K_i^{ROH})_{H_5O_2^+} = -3.77; \quad \lg \left.\frac{k_{true}}{K_i^{ROH}}\right|_{HA} = -2.44.$$

Table 9. Kinetics of the dehydration of β-hydroxy-β-(*p*-methoxyphenyl)propionic acid at 45 °C [the values of k_{dehydr} (min^{-1}) were taken from Noyce et al.[48]].

$[H_2SO_4]$, wt.%	$\lg k_{dehydr}$	$\lg(k_{dehydr}/h_0a_{H_2O})$
1.0	−2.59	−1.56
4.8	−1.68	−1.66
9.25	−1.41	−1.52
16.2	−0.81	−1.55
18.7	−0.69	−1.60
20.6	−0.62	−1.47
22.3	−0.39	−1.42
24.85	−0.18	−1.45

The dehydration reactions in sulphuric acid solutions of an equilibrium mixture of dimethylvinylmethanol and dimethylallyl alcohol and the hydration reaction of isoprene (Table 10)[50] proceed via two pathways: via the formation of an RC with $a_\delta = h_0a_{H_2O}$ and with $a_\delta = a_{H_2SO_4}a_{H_2O}$:



When the composition of the medium is varied, k_{dehydr} changes in accordance with the equation

$$k_{dehydr} = k_{dehydr}^{H_5O_2^+} h_0 a_{H_2O} + k_{dehydr}^{HA.H_2O} a_{H_2SO_4} a_{H_2O}.$$

The linearity of the relation presented in Fig. 1, where $k_{dehydr}/h_0\,a_{H_2O}$ is plotted against $a_{H_2SO_4}/h_0$, confirms the applicability of this equation in the given instance.

The quantity k_{dehydr} for the highest (in the range investigated) H_2SO_4 concentration of 35.11% proved to be significantly lower than expected according to the experimental data for less concentrated acid solutions. This can be explained by the conversion of a large proportion of the unsaturated alcohols into the ionised form.

As noted above, Eqns. (7) and (9) were derived for the case where the degrees of conversion of the ROH and the UC into the ionised form and the RC are low. If the degree of their ionisation is significant, then, provided that only one reaction pathway is retained, these formulae must be supplemented by a multiplier taking into account the concentration of the ionised forms: $1/(1 + \sum a_\delta/K_\delta^i)$, where K_δ^i denotes the equilibrium constants of the formation reactions of the ionised forms.

Table 10. Kinetics of the dehydration of the equilibrium mixture of dimethylvinylmethanol and dimethylallyl alcohol and the hydration of isoprene [the values of k_{hydr} (min^{-1}) and k_{dehydr} (min^{-1}) were taken from Osipova et al.[50]].

$[H_2SO_4]$, wt.%	$\lg k_{hydr}$	$\lg k_{dehydr}$	$c^\infty_{ROH}/c^\infty_{UC}$
4.3	−2.82	−4.02	15.8
7.05	−2.70	−3.89	15.4
10.08	−2.29	−3.48	15.4
15.0	−1.88	−3.05	14.9
15.0	−1.95	−3.12	14.9
19.6	−1.44	−2.59	14.3
20.0	−1.46	−2.62	14.3
20.0	−1.43	−2.58	14.3
24.9	−1.05	−2.15	13.2
27.46	−0.86	−1.96	12.8
30.02	−0.64	−1.72	12.1
32.47	−0.41	−1.47	11.3
35.11	−0.15	−1.18	10.8

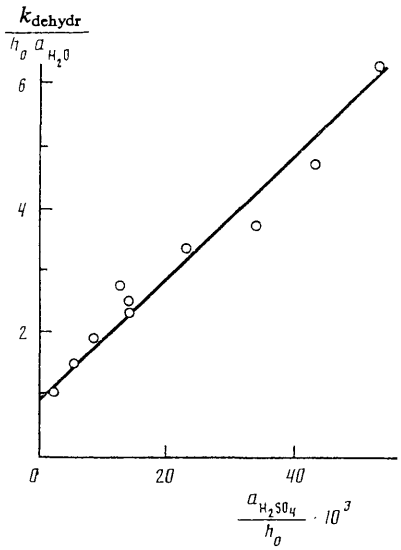


Figure 1. The influence of the H_2SO_4 concentration on k_{dehydr} for the equilibrium mixture of dimethylvinylmethanol and dimethylallyl alcohol (according to the data of Osipova et al.[50]).

The examples presented naturally do not cover all the possible mechanisms of the alcohol dehydration and UC hydration reactions. An illustration may be provided by the dehydration of β-hydroxyketones in acid solutions. Investigators have drawn attention to the fact that substituents in the benzene ring have little influence on the rate of dehydration of β-hydroxyketones.[51] On these grounds, they concluded that the atoms of the benzene ring remote from the reaction centre participate in the rate-limiting stage of the dehydration of these substances and that in certain cases the rate-limiting stage is enolisation. The dependence of k_{dehydr} on the acid concentration in aqueous solution confirms this hypothesis. It has been shown[52] that, when the acid concentration is varied, the enolisation rate constants k_{eff} for acetone varies in accordance with the equation

$$k_{eff} = k_1 c_{H_3O_2^+} + k_2 c_{H_3O_2^+} c_{A^-}, \quad (19)$$

where k_1 and k_2 are respectively the rate constants for pathways with participation of the $H_5O_2^+$ ion and with participation of $H_5O_2^+ + A^-$.

Eqn. (19) is applicable also to the description of the influence of the medium on k_{dehydr} for certain β-hydroxyketones. For example, only the second pathway operates in the dehydration of 4-hydroxy-4-(*p*-nitrophenyl)-2-butanone (Table 11) in the H_2SO_4 concentration range 22.1 − 51.0%. The RC concentration is determined by that of the ions $H_5O_2^+$ and HSO_4^-, so that in this reaction $k_1 = 0$ and $a_\delta = c_{H_3O_2^+} c_{A^-}$.

Table 11. Kinetics of the dehydration of 4-hydroxy-4-(*p*-nitrophenyl)-2-butanone at 25 °C (the values of k_{dehydr} were taken from Noyce and Reed[51]].

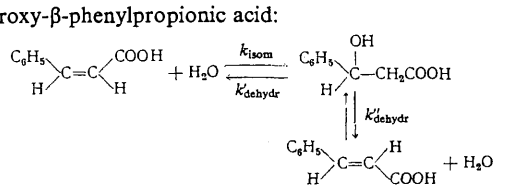
$[H_2SO_4]$, wt.%	$[H_2SO_4]$, M	$10^3\, k_{dehydr}$, min^{-1}	$10^4(k_{dehydr}/c_{H_3O_2^+} c_{A^-})$, $litre^2\, mol^{-2}\, min^{-1}$
9.45	1.02	0.095	9.2
22.1	2.59	0.36	5.4
36.25	3.75	0.74	5.3
41.7	5.61	1.70	5.4
51.0	7.30	3.46	6.5

Note. The degree of dissociation of the HSO_4^- anions may be neglected in the experimental range. In the calculation, it was assumed that c_{A^-} and $c_{H_3O_2^+}$ are numerically equal to the analytical molar concentration of the acid, since the dissociation constant of the HSO_4^- ions is 1.2×10^{-2} [Dobos (Ref. 53, p. 131)].

Judging from the experimental data,[51] when the nitro-group in the *para*-position in the benzene ring is replaced by the methoxy-group, the reaction mechanism changes and the influence of the medium on k_{dehydr} is determined by the functions $a_\delta = a_{H_3O_2^+} = h_0 a_{H_2O}$ and $a_\delta = a_{H_2SO_4} a_{H_2O}$.

In the determination of the reaction mechanism from the dependence of the effective rate constant on the function a_δ, characterising the ionising capacity of the medium, account must be taken of the fact that in the experimental acid concentration range it is possible to select several functions a_δ varying in the same way. This hinders the choice of the reaction mechanism. In order to solve the problem, it is essential to measure the rate constants over wider acid concentration and temperature ranges and to determine the influence of the medium on the activity coefficients of the UC and the corresponding alcohol. If even these experiments do not provide an unambiguous answer, it is necessary to select such a function and hence the reaction mechanism which agrees best with results obtained by other methods. As an example, we shall

examine the isomerisation of *cis*-cinnamic acid in H_2SO_4 at 45 °C to *trans*-cinnamic acid.[54] In this reaction, the intermediate is β-hydroxy-β-phenylpropionic acid:



The rate-limiting stage of the isomerisation reaction is the hydration of *cis*-cinnamic acid, since the rate constant for the hydration of β-hydroxy-β-phenyl-propionic acid is much greater than k_{isom}. Consequently k_{isom} is the rate constant for the hydration of *cis*-cinnamic acid. The data in Table 12 show that in the range 38.43–69.88% H_2SO_4 the quantity $\lg(k_{isom}/a_{H_2SO_4}a_{H_2O})$ is constant within the limits of the error of the measurements, while $\lg(k_{isom}/h_0)$ varies, albeit only slightly. In order to solve the problem of the composition of the RC in this reaction, it is essential to have information about the dependence of f_{UC}/f_{ROH} on the concentration of the catalyst in solution. Unfortunately, such data were not provided in the above study.[54] If it is found that the ratio f_{UC}/f_{ROH} does not change, it will be necessary to conclude that the RC in the given instance is a complex consisting of a molecule of β-hydroxy-β-phenylpropionic acid and a molecule of H_2SO_4 (or *cis*-cinnamic acid, H_2SO_4, and H_2O). On the other hand, if the ratio $(f_{UC}/f_{ROH})a_{H_2O}$ is constant, this will imply that the RC is formed from a molecule of β-hydroxy-β-phenylpropionic acid and the ion pair $H_3O^+.HSO_4^-$.

Table 12. Kinetics of the isomerisation of *cis*-cinnamic acid in aqueous H_2SO_4 solutions at 45 °C [the values of k_{isom} (min^{-1}) were taken from Noyce et al.[54]].

$[H_2SO_4]$, wt.%	$\lg k_{isom}$	$\lg a_{H_2SO_4}$	H_0	$\lg a_{H_2O}$	$\lg(k_{isom}/h_0)$	$\lg(k_{isom}/a_{H_2SO_4}a_{H_2O})$
38.43	−4.84	0.89	−2.21	−0.22	−7.05	−5.51
46.84	−4.10	1.90	−2.89	−0.37	−6.89	−5.63
51.87	−3.55	2.53	−3.30	−0.49	−6.85	−5.59
58.05	−3.01	3.40	−3.90	−0.68	−6.91	−5.73
62.80	−2.44	4.11	−4.45	−0.88	−6.89	−5.67
67.92	−1.87	4.88	−5.18	−1.13	−7.05	−5.62
69.00	−1.71	5.03	−5.33	−1.20	−7.04	−5.54
69.88	−1.59	5.16	−5.47	−1.24	−7.06	−5.51
75.95	−0.82	6.10	−6.40	−1.76	−7.22	−5.16

IV. The mechanism of the exchange of the oxygen atom in alcohols and of the racemisation of optically active alcohols

In order to derive an equation in which account is taken of the influence of the medium on the rate w_{exch} and the rate constants k_{exch} for the exchange of the oxygen atom in alcohols, we express the activity of the RC in terms of the equilibrium constant of its formation reaction, the ROH concentration, and the functions a_δ, as was done above [Eqns. (7) and (8)]:

$$w_{exch} = k_{true}^{exch}\frac{a_{ROH}\,a_\delta}{f^*} = \frac{k_{true}^{exch}}{K_i^{exch}}\,c_{ROH}a_\delta\frac{f_{ROH}}{f^*};$$

$$k_{exch} = \frac{k_{true}^{exch}}{K_i^{exch}}\,a_\delta\frac{f_{ROH}}{f^*};\quad K_i^{exch} = \frac{a_{ROH}\,a_\delta}{a_{ROH.\delta}},$$

where k_{true}^{exch} is the elementary rate constant, K_i^{exch} the equilibrium formation constant, expressed in terms of activities, of the RC in the reaction involving the exchange of the oxygen atom. We believe that, after a correct choice of the function a_δ, the multiplier f_{ROH}/f^* is independent of the acid concentration in the aqueous solution and that

$$k_{exch} = (k_{true}^{exch}/K_i^{exch})a_\delta.$$

An equation of this type can also be used to take into account the influence of the medium on the rate constant for the racemisation of optically active alcohols k_{rac}.

Unfortunately, there are few literature data concerning the dependence of k_{exch} and k_{rac} on the acid concentration in aqueous solution, but on the basis of their analysis one can nevertheless reach conclusions about the mechanism of the catalytic action of acids in these reactions.

Measurements have been made[33] of the constants k_{exch} for methanol at 67.2 °C in sulphuric (20.1–69.3%) and perchloric (26.3–59.9%) acids. The methanol concentration in solution was ~0.3 M. The addition of such amounts of the alcohol to the aqueous acid solution has little effect on the degree of protonation of indicators of the nitroaniline series.[55] However, it has been shown[52] that the basicity of the alcohol itself is independent of its concentration in the mixture with water. Therefore, in analysing the above kinetic data,[33] one can use the values of H_0 and a_{H_2O} for aqueous solutions with the same acid concentration (molar ratio).[52]

The influence of the medium on k_{exch} is determined by the function $a_\delta = h_0a_{H_2O}^2$, since, according to experimental data[33] $k_{exch}h_0a_{H_2O}^2 = \text{const}$. (Tables 13 and 14). This means that the activity of the RC can be expressed either in terms of the product of the activities of the non-protonated CH_3OH, the $H_5O_2^+$ ion, and

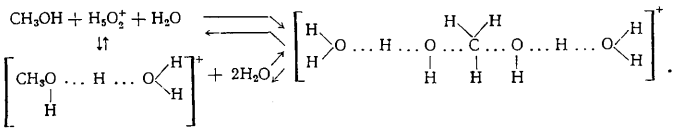
Table 13. Kinetics of the exchange of ^{18}O for ^{16}O in methanol in aqueous H_2SO_4 solutions at 67.2 °C [the values of k_{exch} (min^{-1}) were taken from McClellend[33]].

$[H_2SO_4]$, wt.%	$\lg k_{exch}$	H_0	$\lg a_{H_2O}$	$\lg(k_{exch}/h_0a_{H_2O}^2)$
20.1	−5.99	−0.96	−0.06	−6.83
30.1	−5.47	−1.57	−0.12	−6.80
40.5	−5.07	−2.31	−0.22	−6.94
51.0	−4.63	−3.62	−0.40	−6.85
60.9	−4.26	−4.05	−0.71	−6.89
69.3	−3.93	−5.06	−1.12	−6.75

Table 14. Kinetics of the exchange of ^{18}O for ^{16}O in methanol in aqueous $HClO_4$ solutions at 67.2 °C [the values of k_{exch} (min^{-1}) were taken from McClellend[33]].

$[HClO_4]$, wt.%	$\lg k_{exch}$	H_0	$\lg a_{H_2O}$	$\lg(k_{exch}/h_0a_{H_2O}^2)$
26.3	−5.64	−1.30	−0.09	−6.76
42.1	−4.92	−2.46	−0.26	−6.86
50.5	−4.47	−3.20	−0.44	−6.79
59.9	−3.95	−4.63	−0.89	−6.80

water (with a power exponent of unity) or in terms of the product of the activity of the protonated CH_3OH and the square of the activity of water. The equation of the formation reaction of such RC is



The participation of two water molecules is essential for the intermediate (RC) to have a symmetrical structure. In this RC, the carbon atom is bound covalently to three hydrogen atoms and two water molecules are coordinated to it on either side.

In sulphuric and perchloric acids, the ratios $\lg(k_{exch}/h_0 a_{H_2O}^2)$ are respectively -6.84 ± 0.1 and -6.80 ± 0.06. The similarity of the values of $k_{true}^{exch}/k_i^{exch}$ in these acids constitutes additional confirmation of the reaction mechanism described.

There exist examples of the racemisation of optically active alcohols via this mechanism. For example, the rate constant for the racemisation of 1-methyl-3-phenyl-allyl alcohol in perchloric acid at 25 °C varies in proportion to h_0.[45] The activity of water in solutions with $HClO_4$ concentrations in the range 0.0225–0.333 M is almost constant.

The catalytic action of an acid in alcohol racemisation and oxygen atom exchange reactions is not determined solely by the formation of an RC with $a_\delta = h_0 a_{H_2O}^2$ as in the case of CH_3OH. Thus the influence of the medium on k_{rac} for (+)-β-hydroxy-phenyl-propionic acid in sulphuric acid[47] can be described on the assumption that $a_\delta = a_{H_2SO_4} a_{H_2O}$ (Table 15). In this reaction the activity of the RC should be expressed in terms of the activity of the ROH, the acid, and water with an exponent of unity. The intermediate reactive complex has a symmetrical structure:

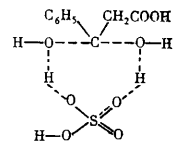


Table 15. Kinetics of the racemisation of (+)-β-hydroxy-β-phenyl-propionic acid in sulphuric acid at 25 °C [the values of k_{rac} (min^{-1}) were taken from Noyce and Lane[47]].

$[H_2SO_4]$, wt.%	$\lg k_{rac}$	$\lg(k_{rac}/a_{H_2SO_4}a_{H_2O})$
39.77	−2.97	−4.24
47.70	−2.17	−4.21
52.03	−1.56	−4.24
58.84	−0.72	−4.18
58.84	−0.72	−4.16
58.84	−0.74	−4.20

The values of $\lg k_{rac}$ at 45 °C have been published.[47] They amount to −1.87 and −1.13 in 39.77% and 47% H_2SO_4 solutions (the k_{rac} are expressed in min^{-1}). Calculation shows that $\lg(k_{rac}/a_{H_2SO_4}a_{H_2O}) = -2.69 \pm 0.01$ at 45 °C and -4.20 ± 0.04 at 25 °C; the temperature dependence of k_{true}^{rac}/K_i^{rac} is characterised by the quantity 137 J mol^{-1}.

In the oxygen atom exchange and 1-phenylethanol racemisation reactions in perchloric acid,[56] the pathways with $a_\delta = h_0 a_{H_2O}^2$ and $a_\delta = a_{HClO_4} a_{H_2O}$ have been observed. The values of k_{rac} for 1-phenylethanol at 30.4 °C in the $HClO_4$ concentration range 0.0172–1.00 M have been published;[56] in 0.0472 and 0.0826 M $HClO_4$ solutions, the ratios k_{exch}/k_{rac} are respectively 0.84 and 0.82. In the concentration range 0.02–0.47 M, the constants k_{rac} in hydrochloric, hydrobromic, and perchloric acids are almost identical. In the acid concentration range 0.0172–1.0 M, k_{rac} is described by the equation

$$k_{rac} = \left(\frac{k_{true}^{rac}}{K_i^{rac}}\right)_{h_0} h_0 a_{H_2O}^2 + \left(\frac{k_{true}^{rac}}{K_i^{rac}}\right)_{HA.H_2O} a_{HClO_4} a_{H_2O}. \qquad (20)$$

Fig. 2 presents experimental data for the influence of the medium on the rate constant for the racemisation of 1-phenylethanol.[56]

It follows from the analysis of the kinetic data described that the alkene hydration and alcohol dehydration reactions proceed via a synchronous mechanism without the particpation of "classical" carbonium ions.

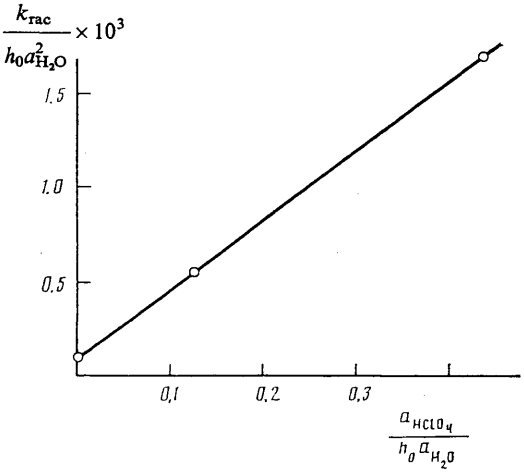


Figure 2. The application of Eqn. (20) to describe the influence of the medium on k_{rac} for 1-phenylethanol (according to the data of Grunwald et al.[56]).

In order to increase the solubility of the reactants, ethanol was added to the acid solution in a number of investigations (see, for example, the studies of Noyce and co-workers[57–59]). The acid concentration and the composition of the mixed water–ethanol solvent (the alcohol/water molar ratio) were varied simultaneously. In the present review, such data are not analysed because it is impossible to take into account the influence of the alcohol on the ionising properties of the solution.

In the analysis of kinetic data, we used the known values of H_0 for sulphuric acid,[60] concentrated perchloric acid solutions at 25 °C,[61] and dilute solutions of perchloric acid[62] and nitric acid at 20 °C.[63] The acitivities $a_{H_2SO_4}$ of concentrated sulphuric acid solutions at 25 °C were taken from Giauque et al.,[64] the activities of dilute sulphuric acid solutions (up to 30 wt.%) were calculated using the values of $\gamma_\pm$ from Dobos,[53] and the activities a_{H_2O} in sulphuric acid were taken from Giauque et al.[64] The activities $a_{H_2SO_4}$ in solutions with acid concentrations up to 60 wt.% at 45 °C were

calculated from the values of $\gamma_{\pm}$ at this temperature, which were found using the relation $\lg \gamma_{\pm} = f(1/T)$ for the range 25–60 °C, quoted by Dobos.[53] The activities a_{H_2O} in perchloric acid at 25 °C were taken from Landolt and Börnstein.[65]

V. Conclusion

The above analysis of kinetic data shows convincingly that, for the determination of the detailed mechanism of the hydration of alkenes in aqueous solutions of acids, it is necessary to know not only the values of k_{hydr} for the alkene but also those of k_{dehydr} for the corresponding alcohol over a wide range of acid concentrations. The composition of the RC in the alcohol dehydration reactions and in the hydration reactions of the corresponding alkenes can be found from the dependence of k_{dehydr} on the parameters of the medium characterising the ionising capacity of the solution. If the ratio of the equilibrium concentrations of the alcohol and the alkene ($c^{\infty}_{ROH}/c^{\infty}_{UC}$) varies with the acid concentration, then the influence of the medium on k_{hydr} can be determined from the values of k_{dehydr} and the experimental equilibrium concentrations c^{∞}_{ROH} and c^{∞}_{UC}. If this ratio remains unaltered at different acid concentrations in solution then the detailed mechanism can be determined using the dependence of k_{dehydr} and k_{hydr} on the parameters of the ionising capacity of the medium.

When the acid concentration is varied within wide limits, the alkene hydration and alcohol dehydration reactions can proceed via several pathways. Therefore, when account is taken of the influence of substituents on the reactivity of substances in concentrated acid solutions, one must be completely certain that the reactions of these substances proceed via identical mechanisms.

In concentrated aqueous acid solutions, catalysis is effected not only by solvated protons, but also by dissociated acid molecules as well as acid hydrates. Kinetic data for the hydration of UC, the dehydration and racemisation of ROH, and the exchange of the oxygen atom in alcohols are susceptible to a quantitative description on the assumption that in these reactions the RC are complexes of the reactant with the above ions and species in the aqueous acid solution.

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Polymeric composite materials reinforced with polyacrylonitrile fibres

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ABSTRACT. The results of studies of the influence of polyacrylonitrile fibres on structure formation in and the properties of polymeric composite materials are surveyed. The new modification methods which have been developed, studies on the properties, and possible applications of such polymeric composite materials are described.

The bibliography includes 74 references.

Contents

I. Introduction 78
II. Changes in the properties of polyacrylonitrile fibres on formation of polymeric composite materials. 78
III. The structure and physicomechanical properties of polymeric composite materials 79
IV. The possible applications of polymeric composite materials 86

I. Introduction

The needs of the National Economy require the creation of new building and constructional materials which would make it possible to reduce sharply the use of metals in finished articles and would increase the strength and anticorrosion properties of constructions and would reduce their mass.[1]

A tendency towards the replacement of components made of traditional materials (wood, metals, ceramics, and glass) in the construction of buildings by polymeric materials has arisen. The requirement for metal is reduced sharply in the first place in those cases where the operating conditions do not involve the application of high pressures and temperatures and where the finished articles are subject to corrosion. Polymeric composite materials (PCM), which are fairly strong and long-lived and are lighter and more resistant to corrosion and erosion than metals, are promising in this instance.[2]

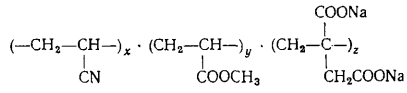
PMC reinforced with chemical fibres (carbon, aramide, etc. fibres) constitute a new class of materials distinguished by a set of valuable properties. PCM based on cheap polyacrylonitrile (PAN), polyester, viscose, polyamide, and other fibres, produced industrially on a large scale, are extremely promising for different branches of the National Economy.[3]

Although the industrial forms of chemical fibres have not been until recently a valuable reinforcing material because of their low strength, relatively low modulus of elasticity, and low heat resistance and thermal stability, nevertheless the possibility of varying their properties widely by modification as well as the set of the specific properties of PCM based on such fibres suggest that in the next few years their application in the reinforcement of plastics will become one of the effective ways of regulating the properties of PCM in accordance with the requirements of different branches of industry.

This review concentrates mainly on PCM reinforced with industrial PAN fibres in view of the increasing scale of their manufacture[4] and their specific properties: low density (1170–1190 kg m^{-3}), low water absorption (0.5–1%), a relatively high thermal stability (200–250 °C), the presence of reactive groups, and a fairly high strength.

Various methods for the modification of both the polymer matrix and the reinforcing fibre system are being developed in order to solve the problem of imparting to PCM the required properties in conformity with their functional purposes.

In the present review, an attempt is made to survey the results of studies and developments concerning different methods for the modification of PCM based on industrial PAN fibres obtained from the ternary copolymer



(0.92% of PAN, 6.3% of methyl acrylate, and 1.7% of sodium itaconate), formed under different conditions, and distinguished by specific physicomechanical properties.

II. Changes in the properties of polyacrylonitrile fibres on formation of polymeric composite materials

The technology of the manufacture of PCM based on chemical fibres differs in many respects from the technology of PCM with mineral fillers, such differences being associated with the specific features of the structure of the chemical fibres and the character of the physicochemical processes occurring at the polymeric fibre–polymeric binder interface.

The formation of PCM on the basis of polymeric fibres is accompanied to a greater or lesser extent—depending on the nature of the selected fibres and binders and the conditions in the pressing of the material (temperature, duration, and pressure)—by the mutual diffusion of the components: of the binder into the fibre and of low-molecular-weight components from the fibre into the polymeric binder.[5] Chemical fibres are structurally inhomogeneous and consist of an oriented high-density shell with an increased degree of crystallinity and a relatively loose core containing crystalline and amorphous sections. Longitudinal folds, 15–200 Å pores, 100–500 Å cracks,[6] and other defects may be present on the surfaces of the fibres.

Since the rate of diffusion into the amorphous regions of the polymers is appreciably higher than the rate of diffusion into the crystalline regions, the components of the binder penetrate the surface layers of the fibres, filling non-uniformly principally the microdefects.[3] This alters the structure of the surface layers of the fibres and hence their properties.[5,7–14]

Depending on the type of fibres and binders chosen, these changes can be both positive and negative.[3,15–18] The change in the supermolecular structure of highly oriented polyamide fibres under the influence of epoxide binders and their components has been investigated[18] by X-ray diffraction.[19] The different character of the interactions of the polyamide fibres based on poly-*p*-phenyleneterephthalamide (PPTA) and on poly-*p*-amidobenzimidazole (PABI) with the components of the EDT-10 and EKhD-MK binders has been established. The chlorine-containing EKhD-MK binder and its principal component, the EKhD resin, impair the structure of the bulk phase of the binders of both types when they interact with them.

The impregnation of nitron, lavsan, and vinol by the latexes of the SKD-1 and SKN-40-1 GP elastomers loosens the fibrillar structures as a result of the diffusion of the elastomer into the surface layer of the fibres.[16]

When technical viscose thread is treated with epoxide and phenolic binders, the strength of the thread is reduced[20] as a result of the penetration of the oligomer molecules into the fibre, the extent of the molecular interaction is diminished, and a disorder in the structure of the fibre is observed.

For poly(vinyl alcohol) (PVA), polyester, and viscose fibres[21] and also for heteroarylene[22] and highly-modular CBM fibres,[23] a plasticisation effect has been observed on treatment with various thermoreactive binders and their components.

After a correct choice of the PCM components and optimum contact conditions between them, it is possible to achieve the improvement of the physicomechanical properties of the fibres. First, under the influence of an epoxide resin accompanied by an increase in temperature up to 180–200 °C, the strength and rigidity of lavsan increase somewhat (by 15–20%). The nature of the hardener in this case has little influence on the rigidity of the fibres, but, up to 100 °C, it does promote an increase in their strength. At temperatures above 100 °C, there is a sharp decrease in the strength of lavsan under the influence of the hardener.

X-Ray diffraction analysis of PAN fibres treated with ED-20 epoxide oligomers, polyethylenepolyamine (PEPA), and a binder based on them showed that impregnation of the PAN fibres leads to the diffusion of the epoxide oligomer and PEPA into the bulk of the fibre, as a result of which the structure[24] and the strength[25] of the fibre change. The change in structure is indicated by the decrease in the intensity of the X-ray reflections: the intensities of the X-ray reflections for unimpregnated PAN fibres and TAN fibre treated with EG-20, PEPA, and binders based on them are respectively, 1, 0.34, 0.41, and 0.08 relative units.

The strength of fibres depends on the nature of the components, the temperature, and the duration of their contact. Thus treatment of PAN fibre with an epoxide oligomer and PEPA for 0.25 h at 80 °C (which corresponds to the PCM pressing conditions) hardly affects the strength and elongation of the fibres, while further increase in temperature and in the duration of treatment of the fibre by the binder components induces its elongation and greatly reduces its strength (Table 1). Consequently, in the making of PCM from chemical fibres, it is necessary to take into account the influence of the binder on the structure and properties of the fibres and to select the appropriate resin–fibre pairs and formation parameters, being guided by the principles formulated by Mashinskaya[3] and Artemenko,[15] which make it possible to bring out most fully the strength properties of reinforced fibres.

Table 1. The change in the strength and elongation of PAN fibres after their treatment with the epoxide oligomer and polyethylene polyamine.

Binder components	Change in properties on heat treatment, %			
	80 °C; 0.25 h		100 °C; 3 h	
	strength	elongation	strength	elongation
ED-20	+8.5	0	−46	+58
PEPA	+1.6	−7.9	−22	+53

III. The structure and physicomechanical properties of polymeric composite materials

1. The influence of polyacrylonitrile fibres on the hardening of polymeric binders

A characteristic feature of PCM reinforced with polymeric fibres is the presence of a diffuse transition layer on the polymeric binder—polymeric fibre interface, arising as a result of the different rates of diffusion of the components of the binder into the amorphous and crystalline sections of the fibres.[5,7–10]

The structure and properties of this layer differ from those of the PCM component. Their different structural organisations are characterised by different molecular mobilities, which is reflected in the rates of relaxation processes.

For example, it has been shown[26] that new levels of structural organisation arise in the bulk phase of an organoplastic based on very strong organic fibres and the epoxyphenol binder. Their molecular mobility is manifested by α'_1- and α'_2–relaxation processes in the region of 453 and 503 K respectively (Fig. 1). The manifestation of a multiplicity of relaxation processes in organoplastics is caused, according to the authors, by the presence of four macroscopic structural organisation levels associated with the binder in the bulk phase of the plastic and in the region remote from the surface of the fibre (α_1), with the binder at the surface of the fibre (α'_1), with the surface layer of the reinforcing organic fibre (α'_2) modified by the diffusing component of the binder, and with the structure of the fibre core (α_2).

Under the influence of the fibres, the conformations of the binder molecules in the transition layer differ from the conformations in the bulk of the polymer, which leads to a non-monotonic variation of the packing density of the macromolecules and going away from the interface.[10] The increase in the order of the arrangement of the epoxide oligomer under the influence of the fibre during the hardening process is confirmed by the increase in the density of the PCM from 1162 to 1319 kg m^{-2} [27] and by the presence on the surface of the fibrous filler of a macrolattice repeating its layered organisation.[25,28] Thus when the fibre is impregnated with the epoxide binder, a diffuse transition layer arises at the fibre–resin interface. The orientation of the globular resin formations at the

surface of the PAN fibre and a decrease in the size of the globules can then be clearly seen. Furthermore, on the fibre (in a unidirectional PCM) the macromolecules of the epoxide binder are oriented on the fibre surface, while in the bulk of the polymer they have a globular structure, which indicates the influence of the surface of the fibre on structure formation in the binder.

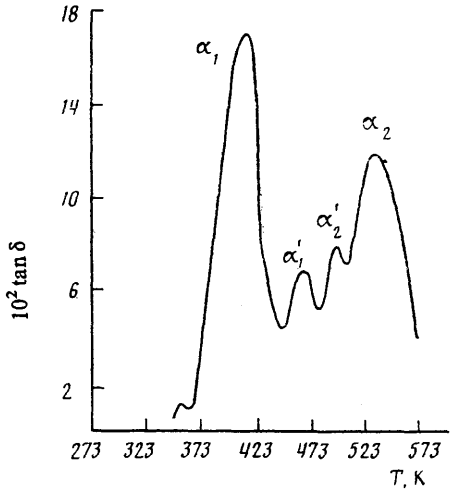


Figure 1. Temperature dependence of the mechanical losses coefficient tan δ of an organic plastic based on an epoxyphenolic binder.

Yet another cause of the formation of a transition layer is the adsorption of one component on the surface of another.[29] A change in the concentration of the cross-linking agent (PEPA) on the surface of the filler as a function of the nature of the chemical fibre has been demonstrated.[30,31] The redistribution of PEPA in the epoxide binder takes place as a result of its selective sorption by chemical fibres.

The structural changes occurring in the binder under the influence of polymeric fibres cannot fail to influence the kinetic parameters of the binder hardening process.

It has been shown[15,29–34] that the introduction of chemical fibres into polymeric binders affects the kinetics of the hardening of the latter in different ways: acetate, polypropylene, and polyamide fibres accelerate while modified viscose fibres retard the hardening process. The retarding effect of the viscose fibre on the hardening of anilinophenol-formaldehyde resin can be explained by the large surface area of the viscose fibre with active hydroxy-groups promoting the sorption of the oligomer and its fairly strong retention on the surface of the fibre. Part of the reactive groups of the oligomer blocked in this way do not participate in the formation of the three-dimensional structure, which diminishes the rate of reaction and lowers the degree of hardening of the polymer.

Lavsan and PAN have a dual effect on polymeric binders. Lavsan retards the hardening of the phenolic binder at 120–140 °C, while at 170 °C it accelerates it. The influence of the PAN fibre is determined by its content in the composition. The introduction of small amounts (up to 5 wt.%) of the PAN fibre into the epoxide binder accelerates the hardening process, while following an increase in its content to 20 wt.% and above (50 wt.%) the formation of the three-dimensional network is retarded both for the epoxide[30] and for the phenolic binders (Fig. 2). Fig. 2 shows that staple fibre exhibits the greatest inhibiting effect, which is due to its high sorption capacity (the specific surfaces of staple fibre and technical twisted cord, determined by gas chromatography, are respectively 7.4 and 4.6 $m^2 g^{-1}$).

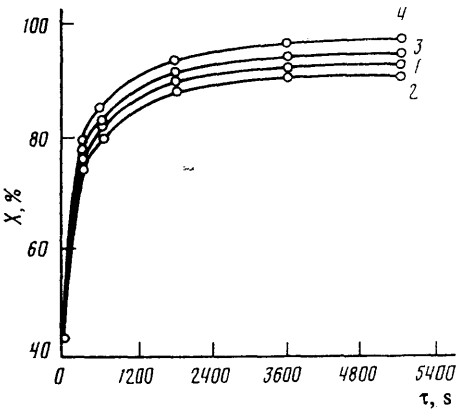


Figure 2. The influence of staple (curves *1* and *2*) and technical PAN fibre on the degree of hardening *X* of SF-342A resin: (*4*) unfilled resin; (*1*) and (*3*) PCM based on PAN fibre (50 wt.%) washed free of the lubricant; (*2*) ditto for the unwashed PCM.

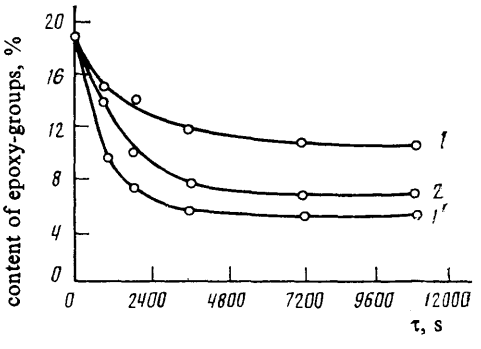


Figure 3. The influence of PAN fibre and temperature on the content of epoxy-groups in an epoxide oligomer: (*1*) and (*1'*) ED-20; (*2*) PCM based on PAN fibre (10 wt.%) [(*1*) and (*2*) at 20 °C; (*1'*) at 100 °C].

The rate and degree of hardening are also influenced by factors such as temperature and pressure.[15,24,33] An increase in temperature from 20° to 100 °C accelerates the hardening of the epoxide binder (Fig. 3). Thus the residual content of epoxy-groups 900 s after the start of the polycondensation process is 14.4% at (20 °C) and 9.8% (100 °C), while 7200 s from the start of the polycondensation process the residual contents are 11.6% (20 °C) and 5.2% (100 °C). The

introduction of PAN fibre into the composition also diminishes the content of epoxy-groups. When 7200 s has elapsed from the start of the polycondensation process, their residual content in the unfilled binder is 11.6%, while in PCM it is 6.8%, which indicates the influence of the fibre on the degree of cross-linking of the epoxide binder.

Thus, by altering the formation parameters and the amount of fibre in the composition, it is possible to regulate specifically the topological structure of the polymeric matrix and hence the properties of the PCM.

2. Methods for the modification of polymeric composite materials based on polyacrylonitrile fibres

Under the conditions of the dynamic scientific and technological development of the National Economy, the regulation of the properties of polymeric composite materials is important in order to meet to the optimum extent technological, operating, and economical requirements of industry. The properties of PCM are regulated by the formation of their specific chemical and physical structure, which is achieved by the modification, using various methods, of both the polymeric matrix and of the reinforcing filler.

Various PCM ensure a wide range of valuable properties—chemical stability, electrical conductivity, mechanical strength, etc. There is much scope for the improvement of the properties of PCM.

One of the most important factors influencing the properties of PCM is internal stresses arising both in the bulk of the binder and, especially, at the binder–chemical fibre interface, caused by the differences between the temperature coefficients of the linear expansion of the polymer and the filler and also by the contraction of the binder during the hardening process.[35,36]

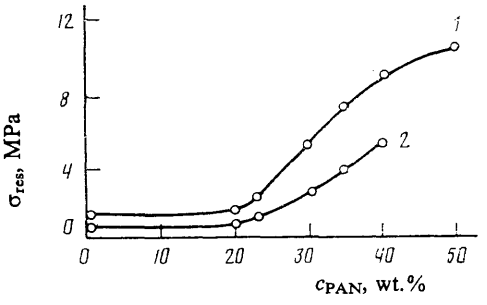


Figure 4. Dependence of the residual internal stress in the initial (curve *1*) and Thiokol-plasticised (curve *2*) composite material on the content of PAN fibre.

The residual internal stresses in the PCM reinforced with PAN fibres have been determined by the polarisation-optical method[37] on model PCM specimens containing between 0.5 and 50 wt.% of the fibre and consisting of transparent films 0.1–0.3 mm thick.

It has been established[25] that a more strained structure compared with the structure of the unfilled resin is produced in epoxide compositions under the influence of the PAN fibre: the introduction of 50 wt.% of PAN fibre into the composition increases by a factor of more than 5 the residual internal stresses [for the unfilled resin and the PCM, the internal stresses amount respectively to 1.8 and 10.3 MPa (Fig. 4, curve *1*)]. This is associated with the fact that fibres have a negative linear expansion coefficient, while the polymeric binder has a positive coefficient. The rigid compression of the fibres by the polymeric matrix prevents the free variation of the volume of the binder during its hardening.

As a rule, the introduction of different plasticisers facilitates the occurrence of relaxation processes in the polymer network being formed, which reduces the residual stresses.[38–40]

A polysulphide rubber (Thiokol) is an effective plasticiser for PCM reinforced with PAN fibre. The introduction of 15 wt.% of Thiokol into the composition makes it possible to reduce greatly the residual internal stresses (Fig. 4, curve *2*)[25] and, with increase in the content of the fibre in the composition, the influence of Thiokol on the internal stresses is enhanced.

The diminution of the residual internal stresses in the PCM following the introduction of Thiokol entails an increase in the impact and water resistance of epoxide PCM and in their strength (Table 2).[41] The phenomenon of "antiplasticisation", expressed by an increase in the bending strength (σ_b) and tensile strength (σ_t) by a factor of 1.2, in impact strength (a_{sp}) and the modulus of elasticity (E_e) by a factor of 1.5, and in elasticity ε by a factor of 1.8 is observed for such systems.[42]

Table 2. The influence of the plasticisation of the epoxide oligomer on the physicochemical characteristics of the PCM.

Plasticiser	Content of plasticiser, wt.%	Physicomechanical properties of PCM					
		σ_s, MPa	σ_b, MPa	a_{im}, kJ m^{-2}	$10^3 E_e$, MPa	ε_{rel}, %	W, %
Without plasticising agent	0	89	140	50	5.2	4.6	0.3
Dibutyl phthalate	10	60	30*	78	4.4	9.7	0.48
	20	—	60*	110	2.2	11.6	0.9
Thiokol	15	100,6	170	73	7.6	8.3	0.106

* The bending moment corresponding to the bending of the specimen by an amount equivalent to 1.5 times its thickness is presented.

The mechanism of "antiplasticisation" in network polymers, especially in unfilled epoxide binders, has been investigated.[43–46] It was established that "antiplasticisation" is the result of the simultaneous alteration of the structure and properties of the matrix and the plasticiser associated with their compaction, which in fact improves the mechanical and other properties.

For PCM reinforced with PAN fibre and plasticised with Thiokol, the increase in strength characteristics and the decrease in water absorption may be associated with the formation in the individual units of the three-dimensional structures of flexible transverse bridges, which promotes the formation of a more close-packed and less strained structure:

$$2R{-}CH{-}CH_2 + HS{-}R'{-}SH \rightarrow R{-}\underset{OH}{CH}{-}CH_2{-}S{-}R'{-}S{-}CH_2{-}\underset{OH}{CH}{-}R.$$
(the first epoxide group: $R{-}CH(O)CH_2$)

As a result, a better compatibility of such polymeric matrix with the fibre is ensured and the operational effectiveness of the PCM as a whole is improved. This is also indicated by the character of the

break. The plasticised material breaks without the separation of the reinforcing component and of the polymeric matrix at high loads (101 MPa) and for large elongations (8.3%), whereas the usual PCM gives rise to a serrated break for lower loads (90 MPa) and elongations (4.6%).

In the plasticisation with Thiokol of PCM reinforced with caproic thread, an increase in the modulus of elasticity and in strength was not observed.[47] On the contrary, in this case the classical plasticising effect was noted, being manifested by an increase in impact strength and in the relative elongation on rupture and by a decrease in the modulus of elasticity.

Thus the plasticising effect of Thiokol in PCM reinforced with chemical fibres is manifested in different ways depending on the nature of the reinforcing fibres.

The method involving modification with small amounts of additives of different chemical nature has been used in recent years for the specific regulation of the properties of various polymers.[49–59]

The modification of polymers by acting specifically on structure formation processes as a rule extends only over the region of physical transformations and all positive effects are achieved as a result of the change in the character of the intermolecular interaction.[53]

The modification of a PCM reinforced with PAN fibre by the introduction of the optimum (2 wt.%) amount of an alloying additive — oligo-oxypropylene glycol (OOPG) — makes it possible to increase the bending strength of the PCM by 50%, the impact strength by 40%, and the tensile strength by 20% (Fig. 5). The alloying additive, which increases the mobility of the polymer chains, stimulates their closer packing, as a consequence of which the free volume diminishes and the viscosity of the system rises.

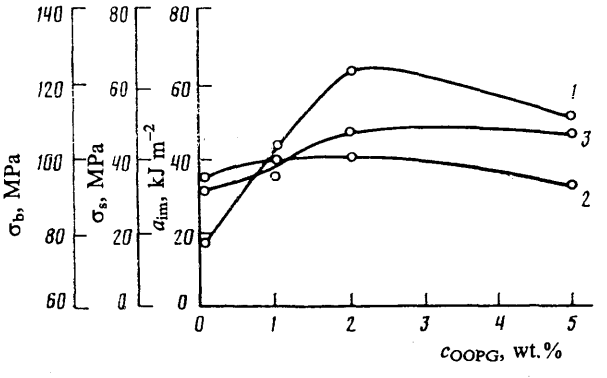


Figure 5. Dependence of the bending (σ_b) (curve *1*) and stretching (σ_s) (curve *2*) breaking stresses and of the impact strength (a_{im}) (curve *3*) of the composite material on the content of the alloying additive.

The increase in the viscosity of the system under the influence of the alloying additive is indicated by the fact that the capacity of the modified oligomer for wetting (determined by the capillary rise method[53]) is impaired.[25]

Furthermore, PCM containing 2 wt.% of oligooxypropylene glycol swells much less in acetone compared with the initial material: the equilibrium degrees of swelling of the modified and unmodified PCM are 15 and 225 mg g^{-1} respectively.

The results obtained show that the modification of PCM reinforced with PAN fibre and small amounts of added organic substances, in particular oligooxypropylene glycol, makes it possible to increase the strength of the material, probably as a result of the better compatibility of the polymeric matrix and the reinforcing fibre.

One of the disadvantages of PCM based on PAN fibres is high combustibility, which limits their applications in branches of industry such as aeroplane construction, building, etc.

The possibility of reducing the combustibility of PCM based on PAN fibres by introducing into them a ternary system comprising bromine-, chlorine-, and phosphorus-containing compounds has been demonstrated.[53] It was established that the efficiency of the modifying additives (combustion inhibitors) is greater if they are introduced into the reinforcing fibre and not into the polymeric binder.

The decrease in the combustibility of such PCM leads to additional possibilities for their use in various branches of industry. Different inorganic additives, in particular antifriction and other additives (graphite, carbon black, molybdenum disulphide, metal powders, etc.) are used nowadays to modify PCM in order to impart to them specific properties.[55,56] However, in most cases the introduction of disperse carriers lowers the strength of the compositions.[57] One of the ways of simultaneously increasing the strength and of improving the antifriction properties of polymeric materials for the manufacture of various sliding components involves the use of hybrid compositions containing both fibrous and disperse fillers.[58] The modification of polymeric materials by such hybrid compositions impart to the PCM a series of new specific properties and the cost of the material is also reduced. Thus the introduction of antifriction additives (molybdenum disulphide and graphite) into the PCM based on PAN fibres in an amount up to 5% not only reduces the coefficient of friction μ but also increases the hardness and bending strength of the material[59] (Table 3). Table 3 shows that the replacement of flaky graphite by highly disperse graphite leads to an additional reduction of the coefficient of friction of the PCM and to an increase in its strength and hardness.

Table 3. Dependence of the coefficient of friction and the physicomechanical properties of the PCM on the type and content of additives.

Additive	Content, wt.%	Physicomechanical properties of PCM			μ
		σ_b, MPa	σ_s, MPa	N_B, MPa	
Initial PCM	0	87	67	28	0.25
Molybdenum disulphide	1	103	54	36	0.18
	3	98	53	38	—
	5	83	50	40	—
Flaky graphite EUT-1	1	99	59	30	0.21
	5	72	62	35	0.20
	10	50	56	38	0.18
Highly dispersed graphite	1	132	—	41	0.14
Acetylene carbon black	1	80	64	—	0.2
	5	84	57	—	0.12
	10	57	48	—	0.13

Although a further increase in the content of antifriction additives in PCM (> 5 wt.%) does in fact reduce the coefficient of friction of the materials, yet at the same time it increases the porosity of the PCM and leads to a decrease in their strength.[59,60]

The antifriction properties of PCM reinforced with PAN fibre depend on temperature. On heating such PCM, the coefficient of friction passes through a maximum (Fig. 6) and the maximum value of the coefficient of friction is observed in the region of the glass point of the polymer (100 °C). (Tests were carried out at a slip rate of 7.5×10^{-3} m s^{-1} and a pressure of 1.5 MPa.) This can be explained by the decrease in the hardness of the material, which increases the area of the actual contact. The hardness of the PCM, both initial and of the material containing 1% of molybdenum disulphide, decreases by 76 and 64% respectively on heating to 100 °C.

The fibres present in the surface layer of the specimen exhibit an additional resistance to friction, which is associated with the transition of the PAN from the vitreous to the highly elastic state. Further increase in temperature leads to an appreciable local overheating of the friction surface, entailing partial degradation of the polymer, as a result of which a charred film is produced, playing the role of a lubricant which reduces the coefficient of friction.

PCM containing graphite behaves differently on heating: on raising the temperature, the coefficient of friction hardly changes (Fig. 6, curve *4*). In all probability, the introduction of even small amounts of graphite (in the given instance 1%) promotes the formation on the friction surface of a layer of graphite, which plays the role of a lubricant.

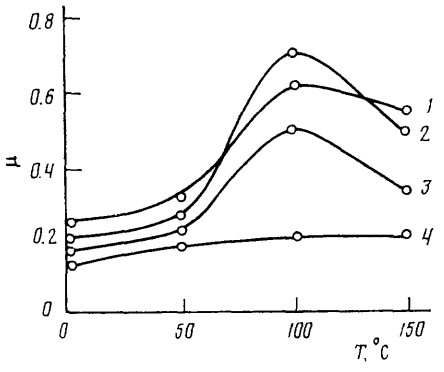


Figure 6. Temperature dependence of the coefficient of friction: (1) initial composite material; (*2*) and (*3*) composite material with molybdenum disulphide [(*2*) reinforcing fibres perpendicular to the friction surface; (*3*) reinforcing fibres parallel to the friction surface]; (*4*) composite material with graphite.

One of the promising aspects of the development of PCM is the creation of hybrid materials, i.e. blends containing three or more components of different chemical composition.[2,61,62] By combining fibrous fillers of different chemical nature, it is possible to obtain PCM with a high resistance to fatigue and the required anisotropy of the properties—in other words it is possible to create materials with the planned properties. The use of polyfibrous fillers makes it possible to obtain materials with the optimum combination of mechanical characteristics, which cannot be achieved in a monoreinforced PCM.

PCM based on inorganic and organic highly modular fibres have been most thoroughly investigated. Questions concerning the classification of the structures, the decomposition mechanisms, and the prospects for the development of such PCM have been described in reviews.[58,62]

One of the features of hybrid PCM is the presence of a hybrid (synergistic) effect. The introduction into PCM reinforced with PAN fibre of viscose (VF) and caproic (CF) fibres, differing from the PAN fibre by their strength and rigidity, makes it possible to reduce the brittleness of the material.

Polyfibrous compositions have been obtained by the joint impregnation of threads of different chemical nature with the binder. The threads were subsequently cut up.

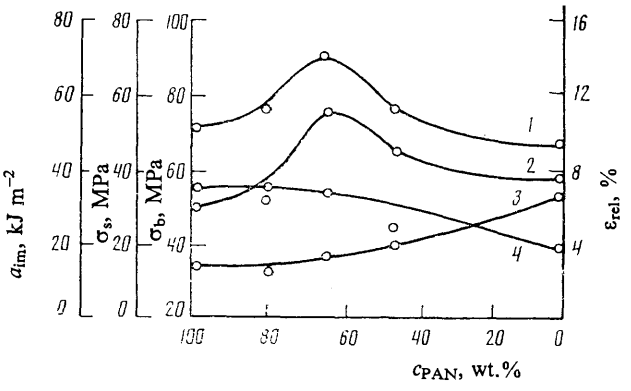


Figure 7. Dependence on the bending (curve *1*) and stretching (curve *4*) breaking stresses, the impact strength (curve *2*), and the relative elongation on rupture (curve *3*) on the ratio of the PAN and caproic fibres in the hybrid filler.

Table 4. Weight losses by hybrid PCM during dynamic heating.

Ratio of PAN and viscose fibres in hybrid filler, wt.%	Weight losses (%) at different temperatures			
	300° C	360° C	400° C	500° C
100:0	10	14	17	25
75:25	12	19	23	32
50:50	14	24	28	38
38:62	13	26	30	41
0:100	35	40	49	59

In the manufacture of polyfibrous compositions based on a mixture of PAN and caproic fibres, the strength of the fibres is not of decisive importance:[63] PCM reinforced with the stronger caproic fibre (62 cN tex^{-1}) has smaller bending and tensile strengths than PCM based on the weaker (41 cN tex^{-1}) PAN fibre as a result of the difference between the elastic properties and the coefficients of thermal expansion of the fibres and the polymeric matrix (Fig. 7).

The combination of these fibres in the PCM in proportions of 65:35 (wt.%) increases appreciably the resistance of the PCM to bending and impact as well as its elasticity. The appearance of a synergistic effect is then observed: the experimental bending and impact strengths of the PCM exceed the additive values on average by 40 and 70%.

A synergistic increase in strength (Fig. 8) and thermal stability (Table 4) has also been noted for polyfibrous compositions containing viscose and PAN fibres taken in equal amounts (50 wt.%) as the reinforcing system: the experimental bending strengths of the PCM exceed by 20% the additive values, while the weight losses, determined by thermogravimetric analysis, exceed the additive values by 5–10%.

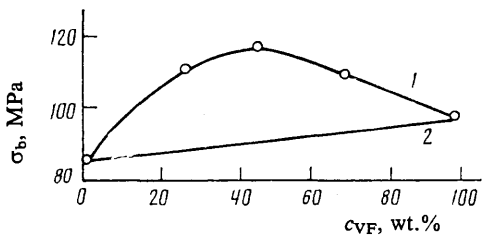


Figure 8. The synergistic increase in the bending strength of the composite material reinforced with a mixture of PAN fibres and viscose thread: (*1*) experimental curve; (*2*) additive curve.

In the preparation of hybrid PCM, the scheme employed for the reinforcement of the polymer matrix with the polyfibrous filler is very important. For example, when fabrics made up of chemical fibres of different chemical nature were impregnated separately with the binder and were subsequently arranged in alternate layers in the composition, the appearance of a synergistic effect was not observed regardless of the type of binder (Table 5).

Table 5. Dependence of the properties of the PCM on the ratio of different fibres in the hybrid filler (on the basis of fabric sheets).

Binder	Ratio of PAN and viscose fibres (wt.%)	Physicomechanical properties of PCM			
		σ_b, MPa	σ_s, MPa	a_{im}, kJ m^{-2}	ε_{rel}, %
Epoxide	100:0	114	58	20	3.8
	50:50	142	88	30	7.0
	0:100	178	130	50	10.2
Phenolic	100:0	104	62	12	4.0
	50:50	119	87	25	5.0
	0:100	190	138	6	—

Thus the combination of PAN fibre with other chemical fibres differing from it in strength and elastic properties makes it possible to increase bending and impact strengths of PCM by 30–40% and their thermal stability by 15–30%.

The fact that the PCM reinforced with PAN fibre combined with viscose fibre has a lower density and a higher resistance to water compared with the PCM reinforced with the viscose fibre alone is fairly important.

A vigorous search has been prosecuted in recent years for new polymeric materials with a high electrical conductivity. Electrically conducting plastics are obtained either by synthesising polymers containing free or mobile electrons, responsible for the semiconducting properties of the plastics, or by introducing electrically conducting additives into polymers.[57] Both powdered and fibrous electrically conducting fillers are usually employed: carbon black, metallic powders, metallic fibres, metallised glass fibre, carbon fibre, etc.[56,57,65,66] However, in order to ensure sufficiently effective electrically conducting properties of the PCM, it is necessary to introduce into the composition an appreciable amount (30–55 wt.%) of a powdered additive, which usually weakens the mechanical properties of the PCM. The introduction into the composition of the PCM of additional carbon and other fibres eliminates this disadvantage but increases significantly the cost of the material (for example, the cost of carbon fibres amounts to between 20 and 200 dollars per kilogram[57]).

A promising aspect of the manufacture of antistatic and electrically conducting PCM involves the introduction into the binder of a fibrous reinforcing filler modified by the method in which metal salts are included (metal salts are incorporated into the structure of the freshly formed fibres).[67,68]

The PCM fibres modified by the inclusion of nickel salts with their subsequent reduction, which ensures a uniform distribution of nickel in the fibre, make it possible to obtain PCM which are fairly strong and have fairly high electrical conductivities in the presence of a very small (2–3 wt.%) metal content.[69]

Table 6. Comparative properties of composite materials based on normal and nickel-containing PAN fibres.

Properties	PAN fibre	
	initial	nickel-containing
Strength of fibre, cN tex^{-1}	22	23
Breaking stress (MPa) in		
bending	110	120—130
stretching	59	54
Impact strength, kJ m^{-2}	16	18
Bulk-phase electrical resistivity, Ωm	$1.9 \cdot 10^{11}$	$4.4 \cdot 10^{6}$
Tangent of dielectric losses angle	0.43	0.004
Electrical strength, kV mm^{-1}	15	3

Thus the introduction of a nickel-containing PAN fibre into an epoxide binder increases the electrical conductivity of the PCM (Table 6). The bulk phase resistivity of such PCM is then reduced compared with the unmodified material by a factor of 10^5 (from 1.9×10^{11} to 4.4×10^6 Ωm), the electrical strength diminishes by a factor of 5, and the tangent of the dielectric losses angle increases by a factor greater than 2. The physicomechanical properties of the modified PCM are then not impaired and a 25% increase in the bending strength is actually observed. The increase in the electrical

conductivity of the PCM indicates the current conducting role of nickel distributed in the fibre in the form of a polyatomic layer. With increase in the weight fraction of the modified fibre in the PCM and also with increase in the nickel content in the fibre structure, the electrical conductivity of the PCM rises as a result of the increased content of the current-conducting component (Table 7). The bulk phase resistivity of the PCM containing 50 and 60 wt.% of the nickel-containing fibre is 4.4 × 10^6 and 8.5 × 10^5 Ωm respectively. The same parameters for the PCM containing fibre with 2.5 and 3.2 wt.% of nickel and respectively 8.5 × 10^5 and 7.1 × 10^3 Ωm.

The dependence of the decrease in the bulk phase resistivity of the PCM on the content of the current-containing component can be explained from the standpoint of the theory of chain conductivity,[65,66] according to which the electrical conductivity is ensured by the significantly greater number of contacts between the electrically conducting elements.

Table 7. Dependence of the electrical properties of the PCM on the content of the nickel-containing fibre (nickel content in fibre 2.5 wt.%).

Content of PAN fibres in PCM, wt.%	Properties of PCM		
	ρ_v, Ωm	E_{br}, kV mm^{-1}	tan α
40	$1.2 \cdot 10^{10}$	7	0.075
50	$4.4 \cdot 10^{6}$	3	0.094
60	$8.5 \cdot 10^{5}$	2	0.90
60*	$7.1 \cdot 10^{3}$	—	—

*The fibre contains 3.2 wt. % of nickel.

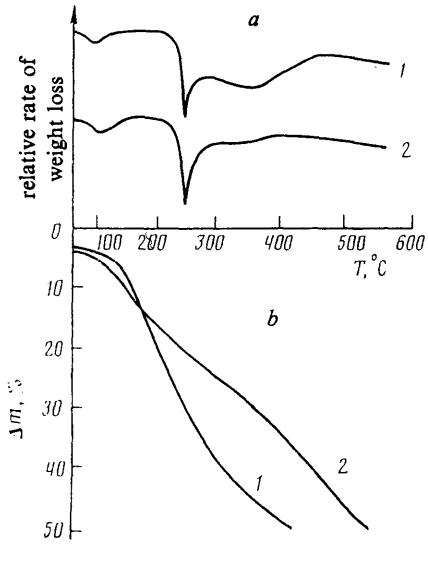


Figure 9. Thermogravimetric analysis of PCM based on the initial (curve *1*) and nickel-containing (curve *2*) PAN fibre: (*a*) relative rate of weight loss; (*b*) weight loss.

Under the influence of the nickel-containing PAN fibre, a more thermally stable PCM structure is formed: the mechanism of the degradation of the modified material is different from that of the initial material and is characterised by the presence of a single peak at 272 °C, whereas the presence of two maxima on the weight loss rate curve is characteristic of the unmodified PCM—at 260° and 348 °C (Fig. 9*a*).[25]

The introduction of nickel into the structure of the PAN fibre increases the stability of the PCM in relation to thermooxidative degradation: the weight losses by the modified PCM are appreciably lower at all temperatures above 160 °C than the weight losses of the initial material (Fig. 9*b*). This is also indicated by the greater stability of the strengths of the PCM after the exposure to different temperatures: the residual strengths of the unmodified and modified PCM after heating the latter for 7 h at 200 °C are respectively 65 and 83% (Fig. 10).

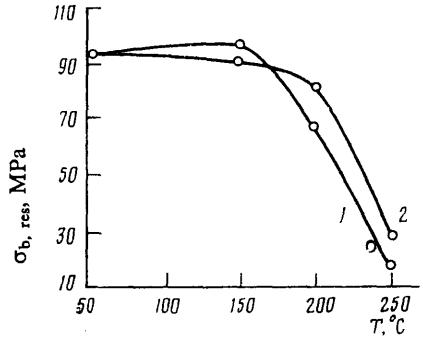


Figure 10. The change in the residual bending strength of the PCM based on the initial (curve *1*) and inclusion-modified (curve *2*) nitron after heating.

On the basis of the data obtained, the PCM reinforced with nickel-containing PAN fibre can be classified as a member of the group of antistatic materials,[65] which can be used to prepare current-conducting elements and also as a facing material for the covering of walls and ceilings.

3. The influence of external media on the properties of polymeric composite materials

The introduction of fibre-fillers into PCM affects not only the character of the structure formation in the filled polymer but also its behaviour on exposure to different external influences. When PCM come into contact with corrosive liquids and their vapours, the latter penetrate into the material owing to the presence of structural defects and the properties of the reinforcing fibres and of the polymeric matrix. Such penetration is accompanied by a change in the weight and strength of the material.

Thus when PCM reinforced with viscose fibre is treated with a reagent capable of inducing appreciable changes only in the polymeric matrix (acetone), the decrease in the strength of the composition is determined by the structure and properties of the three-dimensional network and the hardened polymeric binder.[70]

When PCM is exposed to water, the change in its strength is now limited by the behaviour of the fibres, since the strength of the polymeric matrix, determined by the character of the three-dimensional network, hardly changes under these conditions.

The reinforcement of PCM with hygroscopic viscose fibre, which has a porous surface, leads to appreciable swelling of the PCM in water and to a change in its strength: the decrease in the bending strength and the increase in the mass of the PCM specimens after exposure to water for 1000 h are respectively 30% and 58.3 mg g^{-1}.[7] The modification of the surface of viscose fibre by the chemical grafting of polystyrene, which reduces its sorption capacity, increases the resistance of the PCM to the action of corrosive media.[71]

The same effect is observed when PCM is reinforced with hydrophobic fibres. For example, in phenolic compositions based on kapron and lavsan, the increase in the mass of the material is much smaller than in the PCM reinforced with unmodified viscose fibre.[72]

Table 8. The change in the weight of the specimens after treatment with corrosive media.

Composite material	Medium			
	H_2O	CCl_4	3% H_2SO_4	1% NaOH
Epoxide	−1.4	0.2	−7.5	−1.9
Phenolic	0.4	0.02	0.5	0.4

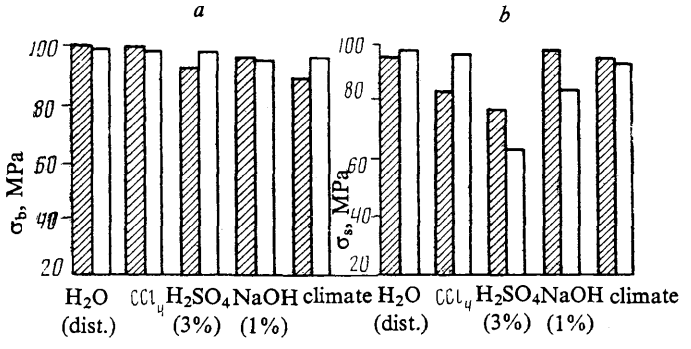


Figure 11. The residual bending strength (*a*) and tensile strength (*b*) of epoxide (shaded columns) and phenolic (unshaded columns) PCM after treatment with corrosive media.

The exposure of PCM based on PAN fibre for a long time (120 days) to corrosive media does not induce an appreciable change in the mass and strength of the specimens (Table 8, Fig. 11). Sulphuric acid is an exception, its action reducing the mass of the epoxide PCM by 7.5% (as a result of some decomposition) and its tensile strength by 22%. The effect of sulphuric acid on phenolic PCM reduces its tensile strength by 36%.

Carbon tetrachloride and dilute alkali do not induce an appreciable change in the strength, mass, and external appearance of such PCM.

The effect of natural climatic factors (climate) during the same period reduces only slightly the strength of the PCM (by 5–10%) (Fig. 11), but there are no changes in the linear dimensions, mass, and external appearance of the specimens under these conditions.

Thus the behaviour of PCM (reinforced with chemical fibre) on treatment with various corrosive media is determined by a whole series of factors, the most important of which are the nature of the fibre and the structure of the PCM surface and also the nature of the binder.

IV. The possible applications of polymeric composite materials

The composite material based on PAN fibre has effective technological properties: the rate of spreading of the moulding material and the fluidity (thickness of the disc), determined by the method of Dyukhin and Stavrov,[73] are respectively 0.25 mm × s^{-1} and 1.6 mm.[74] Articles made from this material have a pleasant external appearance and a shiny surface and can be subjected to all kinds of mechanical treatment: milling, drilling, turning, polishing, etc.

The PCM which have been developed have a set of specific properties: an increased resistance to bending and impact loads, a low density, a fairly high atmospheric and chemical stability, an improved thermal stability, and antifriction properties.

The results obtained show that it is useful to employ PCM based on PAN fibre in chemical machine construction and also as building materials for the protection of constructions against corrosion.

In the building industry, PCM are used to prepare facing materials and sanitary-technical articles, in particular, for the manufacture of various connecting components used in the assembly of pipelines. Articles made of PCM have a number of advantages over metallic articles. These include primarily corrosion resistance and low density.

Industrial tests on facing plates made of PCM reinforced with PAN fibre demonstrated the possibility of using them to cover industrial environments.

No changes in the physicomechanical characteristics of the PCM and its external appearance on treatment with water and acetic acid vapour were observed during the tests.

A modified PCM containing graphite (1%) can be usefully employed as an antifriction material. Tests on experimental specimens (inserts in slip bearings) showed that metal-PTFE inserts can be usefully replaced by inserts made from antifriction PCM. The intrinsic cost of the components is then reduced and their useful operating life is increased. In addition, the possibility of employing PCM with added graphite in dry friction components makes it possible to abandon the use of scarce and expensive lubricating materials.

The PCM which have been developed, reinforced with PAN fibres, can be recommended for the manufacture of components and constructions withstanding impact loads, for example, for the manufacture of the shells of shuttles in looms.

Industrial tests on experimental specimens demonstrated that PCM reinforced with chemical fibres are economical and their application is technically and socially useful. In the first place the intrinsic cost of the material is reduced and in the second it is possible to replace the natural fibres which are still used in technical applications as reinforcing fillers for PCM, for example in the manufacture of blades for looms, textolite, etc.

A polymeric composite material based on nitron, which has effective strength properties, is susceptible to manufacture by modern technology, has a pleasant external appearance, and can be used as a constructional material for the manufacture of various components.

Tests have demonstrated that PCM based on PAN fibre can be usefully employed for the manufacture of bowls for fuel filters. The bowls made from the PCM are light and strong, are oil and petrol resistant, and can successfully replace containers made from metal and AGH-4V material.

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β-Fluoro-substituted aminoacids

V P Kukhar', Yu L Yagupolskii, V A Soloshonok

ABSTRACT. The review gives a systematic account of data concerning the methods of synthesis of α-, β-, and γ-aminoacids containing fluorine atoms in the β-position relative to the amino-group. The interest in these compounds is in many respects due to the fact that most of them have proved to be highly selective irreversible inhibitors of pyridoxal-5-phosphate-dependent enzymes acting via the "suicide-substrate" mechanism. Attention is concentrated on β-fluoro-derivatives of natural α-aminoacids.

The bibliography includes 114 references.

Contents

I. Introduction 89
II. Classical methods of synthesis of β-fluoro-substituted aminoacids 90
III. Special methods of synthesis of β-fluoro-substituted aminoacids 93
IV. Conclusion 100

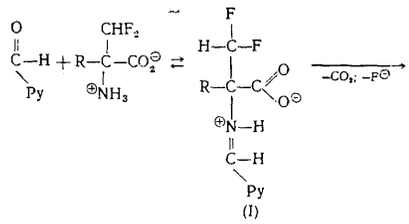
I. Introduction

Even if one disregards the unique importance of aminoacids in the initiation of life on Earth, compounds of this class possess a sufficient number of biological functions to be placed in the forefront of substances without which living organisms could not exist. The synthesis of aminoacids and their organoelement analogues therefore constitutes a most important aspect of modern bioorganic chemistry concerned with the creation of new medicinal preparations and fine biochemicals.

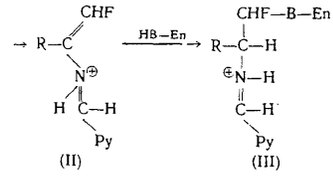
The vigorous development of organofluorine compounds after the 1940s and certain advances in the use of fluorinated analogues of natural products have created objective grounds for the initiation of vigorous research into fluorine-containing aminoacids. At the present time these compounds are one of the most promising types of low-molecular-weight bioregulators.[1]

Analysis of a considerable amount of data on the biological activity of fluoro-substituted aminoacids made it possible to differentiate in the first place compounds which are highly selective irreversible inhibitors of enzymes with the pyridoxal phosphate group, such as aminoacid racemases, transaminases, and decarboxylases. A common structural feature of substances exhibiting the properties of inhibitors of this type was found to be the presence of fluorine atoms in the β-position relative to the amino-group.

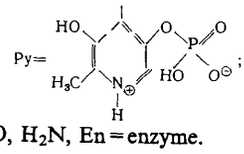
On the basis of numerous studies undertaken to explain the biochemical activity of β-fluoro-substituted aminoacids, a mechanism has been proposed[2–4] whose idea is that the enzyme itself synthesises the substance inhibiting it—the "suicide-substrate". Thus in the case where the substrate of decarboxylase is a β-fluoro-α-aminoacid, the reversible formation reaction of the Schiff base (I) is followed by the irreversible decarboxylation stage with elimination of the fluorine atom from the β-position and the formation of the Michael acceptor (II). The latter reacts with the nucleophilic groups of the enzyme located near the active centre. This reaction is irreversible; the enzyme, bound covalently to the aminoacid residue (III), loses its ability to interact further with the substrate and is deactivated.



(I)



(II) (III)



HB = HO, H_2N, En = enzyme.

The deactivation of transaminases or racemases by β-fluoro-substituted aminoacids also proceeds via an elimination stage or a stage involving activation with respect to the nucleophilic substitution of the fluorine atom with the subsequent chemical binding of the aminoacid residue to the nucleophilic centre of the enzyme. The suppression of the enzymic reaction via the mechanism described above leads to the appearance of bactericidal and other types of biological activity in β-fluoro-substituted aminoacids.[5,6]

The determination of the biochemical mechanism of the inhibition of enzymes by β-fluoro-derivatives of aminoacids has greatly stimulated studies on these compounds.

The syntheses of β-fluoro-substituted aminoacids achieved hitherto are various from the standpoint of both the methods and the initial compounds employed. However, certain types of aminoacids have been obtained using mainly the methods of organic or organofluorine chemistry. This made it possible to differentiate in this review two main sections: the classical and special methods of synthesising β-fluoro-derivatives of aminoacids.

The reviews available in the literature[7,8] deal with the methods of synthesis of all types of fluorine-containing aminoacids, including β-fluoro-derivatives, published up to 1968. Later publications[9–11] deal with the methods of synthesis and biological activity of only

individual types of β-fluoro-substituted aminoacids, for example, such as α-polyfluoromethyl-substituted aminoacids. The present review surveys studies on the synthesis of α-, β-, and γ-aminoacids containing fluorine atoms in the β-position relative to the amino-group, carried out mainly during the last twenty years, earlier sources being referred to when necessary.

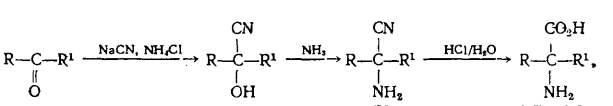
Data on the biological activity of the compounds examined are quoted only in those cases where in the sources referred to the biological activity of the aminoacids is reported together with their synthesis. A number of reviews have been devoted to the biological properties of β-fluoro-substituted aminoacids.[3,4,9–12]

II. Classical methods of synthesis of β-fluoro-substituted aminoacids

Almost all the known methods of synthesis of non-fluorinated aminoacids have been used to obtain their fluorinated analogues. However, only a few of these methods proved to be preparatively valuable and remained of current interest up to the present time. The applicability of the classical methods of synthesis of aminoacids to the series of fluorine-containing compounds is limited by the specific influence of fluorine or perfluoralkyl groups as a result of which many reactions may alter their character during the synthesis. The influence of fluorine atoms next to reaction centres is especially marked. The classical methods have therefore found only limited applications in the synthesis of β-fluoro-derivatives of aminoacids.,

1. Synthesis of β-fluoro-derivatives of aminoacids from fluorine-containing carbonyl compounds

The Strecker synthesis of aminoacids was one of the first used to obtain mono- and di-fluoroaminoacids. However, in contrast to the non-fluorinated ketones, the reactions mainly stop in the first stage—the formation of the corresponding cyanohydrins (IV). Thus a mixture of nitriles of 3-fluoro-2-hydroxyisobutyric and 3-fluoro-2-aminoisobutyric acids in proportions of 13:87 has been obtained from monofluoroacetone, while 3,3′-difluoro-2-hydroxyisobutyric acid has been obtained as the only reaction product from 1,3-difluoroacetone.[13,14]

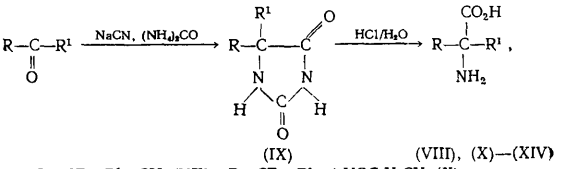


R=CH_2F, $R^1=CH_3$ (VI); $R=R^1=CH_2F$ (VII).

In order to obtain aminoacids, the cyanohydrins (IV) were converted by treatment with ammonia into the aminonitriles (V), from which mono- and di-fluoro-derivatives of α-aminoisobutyric acid (VI) and (VII) were obtained by acid hydrolysis.

3,3,3-Trifluoro-α-aminoisobutyric acid (VIII) was obtained from 3,3,3-trifluoroacetone via a stage involving the formation of 5-methyl-5-trifluoromethylhydantoin (IX), whose yield was 23%.[15]

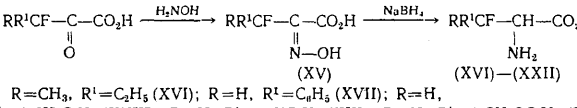
A series of α-trifluoromethylphenylalanines (X)–(XII) have been obtained by the same methods from the corresponding fluorinated ketones. The yield of the hydantoins (IX) formed initially did not exceed 50%.[16] Compounds (X)–(XII) can be used to regulate the level of noradrenalin.



R=CF_3, $R^1=CH_3$ (VIII); R=CF_3, R^1=4-$HOC_6H_4CH_2$ (X);
R=CF_3, R^1=3, 4-$(OH)_2C_6H_3CH_2$ (XI); R=CF_3,
R^1=3, 4, 5-$(OH)_3C_6H_2CH_2$ (XII);
R=CHF_2, R^1=4-$HOC_6H_4CH_2$ (XIII); R=CH_2F,
$R^1=HO_2C(CH_2)_2$ (XIV).

The introduction of ketones containing less electron-accepting mono- and di-fluoromethyl groups into the Bucherer reaction affords the hydantoins (IX) in higher yields. α-Difluoromethyltyrosine (XIII)—an effective hypotensive preparation[17]—and α-fluoromethyl-glutamic acid (XIV)—an irreversible inhibitor of glutamate decarboxylase[18]—were also obtained by this method.

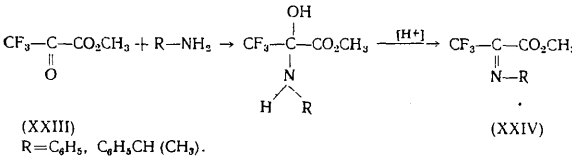
A widely used method of synthesis of aminoacides and amines, based on the reduction of compounds with a C=N bond, has also been employed to synthesise β-fluoro-derivatives of aminoacids. A disadvantage of this method is the low availability of β-fluoro-α-keto-acids. Fluorine-containing ketoacids were introduced into the reaction with hydroxylamine and the corresponding aminoacids were obtained by the subsequent reduction of the oximes (XV) formed. β-Fluoroisoleucine (XVI),[19] a series of β-fluorophenylalanines (XVII)–(XXI), exhibiting antimicrobial and anticancer activities,[20,21] as well as ββ-difluoroaspartic acids (XXII), which is an irreversible inhibitor of aspartate aminotransferase,[22] were obtained by this procedure.



R=CH_3, $R^1=C_2H_5$ (XVI); R=H, $R^1=C_6H_5$ (XVII); R=H,
R^1=4-$CH_3C_3H_4$ (XVIII); R=H, R^1=4-ClC_6H_4 (XIX); R=H, R^1=4-$CH_3OC_6H_4$ (XX);
R=H, R^1=4-$O_2NC_6H_4$ (XXI); R=F, $R^1=HO_2C$ (XXII).

The stereochemical aspects of the formation of *erythro*- and *threo*-β-fluorophenylalanines (XVII)–(XXI) during the reduction of the oximes (XV) have also been investigated in a series of studies[21,23,24] and it has been shown that mainly the *erythro*-isomers of β-fluoro-substituted aminoacids are obtained.

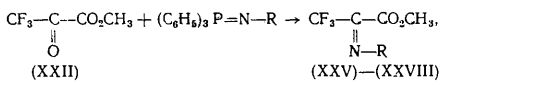
A method of synthesis of trifluoroalanine and of a series of its *N*-alkyl- and *N*-aryl-derivatives from the readily available methyl trifluoropyruvate (XXIII) have been developed recently.[25] The corresponding imines cannot be obtained by the direct interaction of the ketoester (XXIII) with ammonia or amines. An exception is provided by α-phenylethylamine and aniline, whose adducts with the ketoester (XXIII) are dehydrated in the presence of acid catalysts to the corresponding imines (XXIV).



(XXIII)
R=C_6H_5, $C_6H_5CH(CH_3)$.

(XXIV)

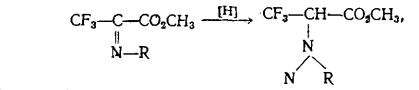
The most general method of synthesis of imines of methyl trifluoropyruvate is the Staudinger reaction, which makes it possible to obtain the imines (XXV)–(XXVIII) in 60–95% yields.



(XXII) (XXV)—(XXVIII)

R = C_6H_5 (XXV), n-C_4H_9 (XXVI); $C_2H_5CH(CH_3)$ (XXVII), CH_3O_2C (XXVIII)

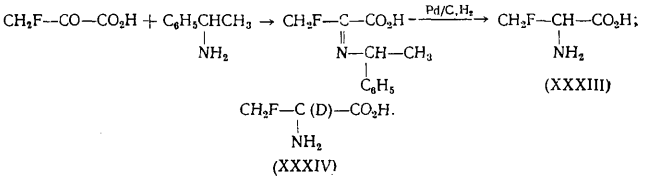
Sodium tetrahydroborate and hydrogen on palladium black have been used to reduce compounds (XXIV), (XXV), (XXVII), and (XXVIII) to the corresponding alanines (XXIX)–(XXXII), but reduction with zinc in acetic or formic acid proved to be the most convenient.



(XXIV), (XXV), (XXVII), (XXVIII) (XXIX)—(XXXII)

R = $C_6H_5CH(CH_3)$ (XXIX); C_6H_5 (XXX), $C_2H_5CH(CH_3)$ (XXXI), CH_3O_2C (XXXII).

The reduction of the optically active *N*-phenylethylimine (XXIV) with various reducing agents proceeds with a slight asymmetric induction (the ratio of the diastereoisomers is 5 : 4). However, in the case of monofluoropyruvic acid the use of the optically active L-α-phenylethylamine makes it possible to achieve the asymmetric synthesis of a highly effective antibacterial agent—3-fluoro-D-alanine (XXXIII)[26]—in accordance with the following scheme:



(XXXIII)

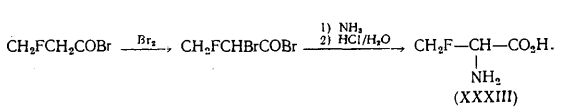
(XXXIV)

A deuteriated analogue of fluoroalanine (XXXIII)—"fludalanine" (XXXIV)—has been obtained by a similar procedure from monofluoropyruvic acid using $NaBD_4$ as the reducing agent.[27]

2. The substitution of the α-halogen atom or the α-hydroxy-group by the amino-group

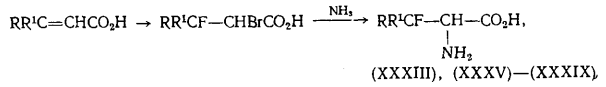
The method of synthesis of aminoacids by the introduction of an amino-group into carboxylic α-halogeno- or α-hydroxy-acids has been used successfully to synthesise a wide variety of fluorine-containing aminoacids.[7,8] However, this method proved to be applicable to the synthesis of β-fluoro-substituted aminoacids only in the case of the monofluoro-derivatives. This is associated with the fact that fluoroalkyl and especially perfluoroalkyl groups hinder nucleophilic substitution in the neighbouring carbon atom.

Thus monofluoroalanine (XXXIII) has been obtained in a low yield from the bromide of 3-fluoropropionic acid by the successive bromination and treatment with ammonia of the bromide of α-bromo-β-fluoropropionic acid formed.[28]



(XXXIII)

Subsequently the method was improved by employing acrylic acid derivatives as the starting compounds.[29] The coupled addition of fluorine and bromine to 3-alkylacrylic acids was carried out by treatment with *N*-bromosuccinimide in liquid hydrogen fluoride with formation of carboxylic α-bromo-β-fluoroacids. The latter were converted into the corresponding aminoacids (XXXIII), and (XXXV)–(XXXIX) in 10–63% yields by treatment with ammonia.

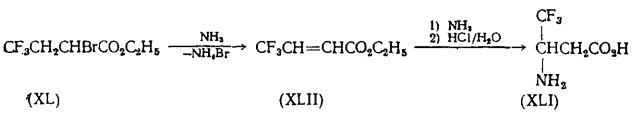


(XXXIII), (XXXV)—(XXXIX)

R = R^1 = H (XXXIII); R = R^1 = CH_3 (XXXV); R = H, R^1 = CH_3 (XXXVI); R = H, R^1 = C_2H_5 (XXXVII); R = H, R^1 = n-C_3H_7 (XXXVIII); R = H, R^1 = n-C_4H_9 (XXXIX).

This method made it possible to increase the yield of fluoroalanine (XXXIII) and to obtain a series of new aliphatic β-fluoro-α-aminoacids with antifungal or antimicrobial activity.[29]

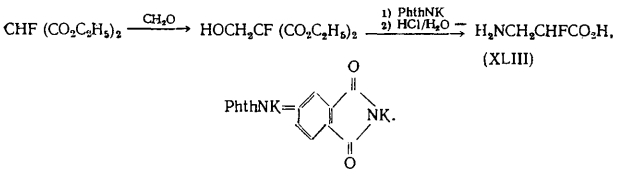
Instead of the expected derivative of 4,4,4-trifluoro-2-aminobutyric acid, the ammonolysis of ethyl 2-bromo-4,4,4-trifluorobutyrate (XL) afforded the β-alanine ester—4,4,4-trifluoro-3-aminobutyric acid (XLI).[30,31]



(XL) (XLII) (XLI)

It was found that, on treatment of the bromo-derivative (XL) with ammonia, hydrogen bromide is split off and ethyl trifluorocrotonate (XLII) is formed, which can be explained by the inductive effect of the trifluoromethyl group, facilitating the elimination of the proton in the β-position. In the next stage of the reaction, ammonia adds in the usual way to the β-carbon atom. The above mechanism of the formation of the β-alanine (XLI) has been confirmed by its synthesis from trifluorocrotonic acid (XLII).[32] Biological tests have shown that β-trifluoromethyl-β-alanine (XLI) possesses antibacterial activity.[32]

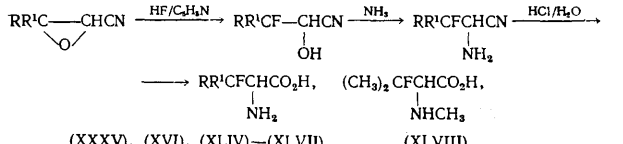
The synthesis of β-fluoro-derivatives of aminoacids with the replacement of the hydroxyl by the amino-group proved successful only in the synthesis of monofluoro-derivatives. α-Fluoro-β-alanine (XLIII), first isolated as a 5-fluorouracil metabolite,[33–35] has been synthesised from diethyl fluoromalonate in accordance with the following scheme:[36]



(XLIII)

α-Fluoro-β-alanine (XLIII) has been synthesised similarly from α-fluoro-β-hydroxypropionic acid.[37]

A general method of synthesis using 2-cyanoepoxides has been developed recently to obtain β-fluoro-α-aminoacids.[38]



(XXXV), (XVI), (XLIV)—(XLVII), (XVII), (XXXVI) (XLVIII)

R = R^1 = CH_3 (XXXV); R = CH_3, R^1 = C_2H_5 (XVI); R = R^1 = C_2H_5 (XLIV); R = H, R^1 = C_6H_5 (XVII); R = CH_3, R^1 = C_6H_5 (XLV); R = H, R^1 = CH_3 (XXXVI); R + R^1 = $(CH_2)_4$ (XLVI); R + R^1 = $(CH_2)_5$ (XLVII).

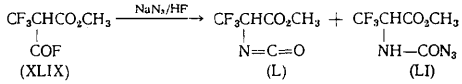
The opening of the epoxide ring with the aid of the Olah reagent (a solution of hydrogen fluoride in pyridine) leads to a high yield of β-fluoro-α-hydroxynitriles, from which the corresponding amino-derivatives were obtained in 13–85% yield by treatment with ammonia in the presence of $MgSO_4$. Hydrolysis of these compounds afforded the free β-fluoro-α-aminoacids (XVI), (XVII), (XXXV), (XXXVI), and (XLIV)–(XLVII).

The use of methylamine in this reaction instead of ammonia made it possible to synthesise the corresponding *N*-methyl derivatives of β-fluoroaminoacids (XLVIII).[38]

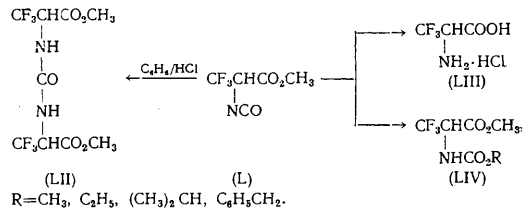
3. Other methods of synthesis of β-fluoro-derivatives of aminoacids

The conversion of the carboxy-group into the amino-group by the Curtius method has been used to obtain α-trifluoromethyl- and α-difluoromethyl-substituted aminoacids.

A method[39] based on the conversion of the fluoride of 2-methoxycarbonyl-3,3,3-trifluoropropionic acid (XLIX) has been proposed for the synthesis of trifluoroalanine. The acid fluoride (XLIX) was converted by treatment with sodium azide or trimethylsilyl azide into the corresponding isocyanate (L). When the initial acid fluoride (XLIX) contains an admixture of hydrogen fluoride, the reaction is complicated by the formation of the carbamoyl azide (LI).

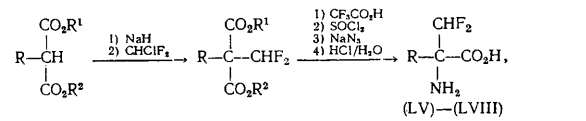


The interaction of the isocyanate (L) with water proceeds in different ways depending on the reaction conditions. Thus hydrolysis of a benzene solution of compound (L) with concentrated hydrochloric acid proceeds with formation of the symmetrical urea (LII). The hydrochloride of trifluoroalanine (LIII) has been obtained by treating the isocyanate (L) with hydrochloric acid in the absence of a solvent.



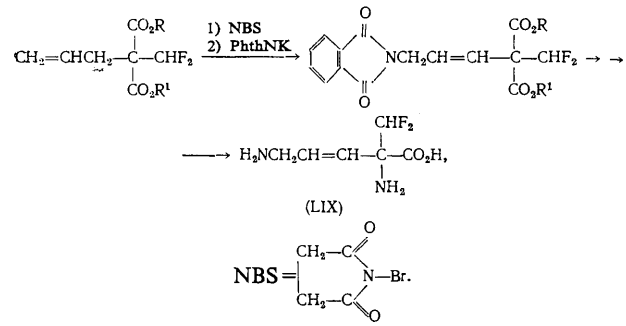
The introduction of the isocyanate (L) into a reaction with alcohols made it possible to obtain the methyl esters of trifluoroalanine (LIV) containing *N*-alkoxycarbonyl groups.

The Curtius reaction has also been used as the key stage in the synthesis of α-difluoromethyl-substituted aminoacids. Treatment of substituted malonates, having two different substituents in the ester groups, with Freon subsequently made it possible to eliminate selectively one of these substituents (OBu^t) by treatment with trifluoroacetic acid. The subsequent treatment of the intermediate acid ethyl malonates with thionyl chloride and sodium azide yielded the corresponding isocyanates, which were hydrolysed to the aminoacids without isolation.[40–42]

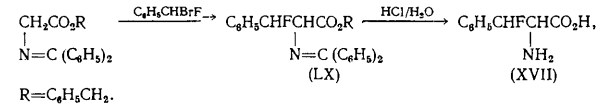


The difluoromethyl derivatives of aspartic acid (LV), alanine (LVI), and phenylalanine (LVII) have been obtained by this method.

By bromination and subsequent replacement of the bromine atom by the phthalamide group, 2-allylmalonic ester has been converted into the protected δ-amino-derivative from which δ-difluoromethyldehydroornithinine (LIX)—an irreversible inhibitor or ornithinine decarboxylase—was obtained in accordance with the scheme presented above.[40]



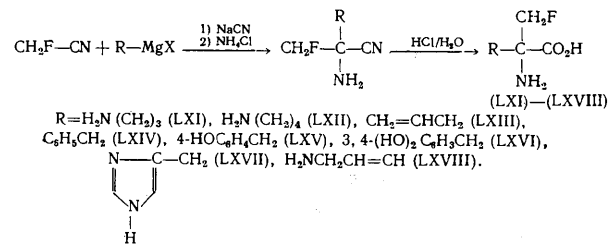
Yet another example of the use of classical methods of synthesis of aminoacids for the preparation of their β-fluorinated analogues is the alkylation of the benzyl ester of *N*-(α-phenylbenzylidene)glycine by bromofluorophenylmethane.[43]



The Schiff base was alkylated in methylene chloride in the presence of $(C_4H_9)_4N^{\oplus}HSO_4^{\ominus}$ and the alkylated product (LX) was obtained in 71% yield. It was hydrolysed to β-fluorophenylalanine (XVII).

The involvement of carboxylic acid nitriles in reactions with organometallic reagents has been rarely used to synthesise non-fluorinated aminoacids. However, in the synthesis of α-monofluoromethyl derivatives of aminoacids, this approach proved to be a successful alternative method of the direct fluoromethylation of the C-anions of protected aminoacids, which will be examined in the next section.

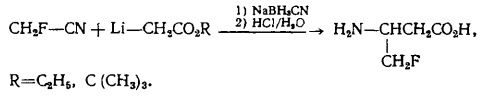
The reactions of monofluoroacetonitrile with organomagnesium reagents have been carried out at −40 °C in solution in tetrahydrofuran. The imines formed under these conditions were treated, without isolation, with sodium cyanide and then ammonium chloride was added.[44,45]



α-Monofluoromethyl-substituted derivatives of ornithine (LXI), lysine (LXII), 2-allylglycine (LXIII), phenylalanine (LXIV), tyrosine (LXV), dihydroxyphenylalanine (LXVI), and histidine (LXVII) were obtained by this method. A patent[45] states that monofluoroornithine (LXI) can be used as an effective antifertility agent.

α-Monofluoromethyldehydroornithine (LXVIII) has been obtained by introducing a functional group into 2-allyl-3-fluoroalanine (LXIII) similarly to the scheme employed for the synthesis of α-difluoromethyldihydroornithine (LX).

The application of lithium derivatives of acetate esters in the reaction of monofluoroacetonitrile made it possible to achieve the synthesis of 3-amino-4-fluorobutyric acid (LXIX)—an inhibitor of γ-aminobutyric acid transaminase.[46]



$R=C_2H_5$, $C(CH_3)_3$.

III. Special methods of synthesis of β-fluoro-substituted aminoacids

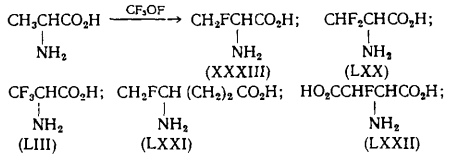
The methods of organofluorine chemistry have been recently used extensively for the synthesis of fluorine-containing aminoacids. The procedures for the introduction of fluorine into the molecules of organic compounds with the aid of elemental fluorine transferring agents, such as trifluoromethyl hypofluorite and perchloryl fluoride and fluorinating agents—antimony trifluoride, sulphur tetrafluoride and its derivatives, as well as metal fluorides (KF, AgF)—proved especially useful.

1. The replacement of hydrogen and halogen atoms and of hydroxy-, mercapto-, and amino-groups by fluorine atoms in the molecules of aminoacids of their derivatives

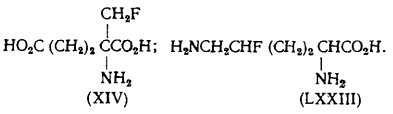
One of the most promising but little used methods of synthesis of fluorine-containing aminoacids involves the direct fluorination of aminoacid molecules. An important disadvantage of this method still remains its low selectivity, as a result of which mixtures of reaction products are formed, which hinders the isolation of the target product.

A synthesis of this type was first achieved in the preparation of 4-fluoroglutamic acid using perchloryl fluoride.[47–49]

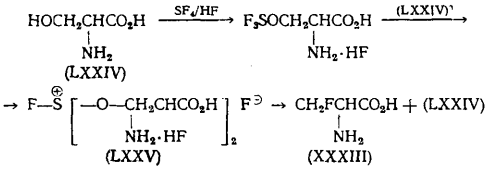
The most effective fluorinating agent for the synthesis of β-fluoro-derivatives of aminoacids is trifluoromethyl hypofluorite.



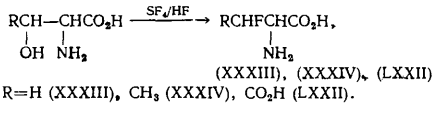
The reactions were carried out under UV irradiation in hydrogen fluoride. Monofluoroalanine (XXXIII),[50–52] difluoroalanine (LXX), trifluoroalanine (LIII),[53] γ-fluoromethyl-γ-aminobutyric acid (LXXI),[54] β-fluoroaspartic acid (LXXVII),[53] and α-fluoromethylglutamic acid (XIV)[55,56] were synthesised in this way from non-fluorinated aminoacids. In the fluorination of lysine with CF_3OF, one of the reaction products was 5-fluorolysine (LXXIII).[57] The lack of selectivity is the main disadvantage of the method.



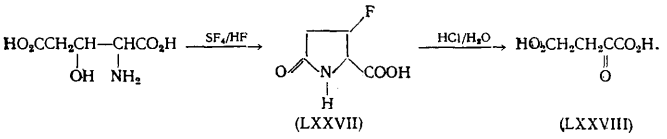
The method involving the replacement of the hydroxy-group by fluorine with the aid of sulphur tetrafluoride or its derivatives, widely used in organofluorine chemistry, has been applied successfully in the synthesis of β-monofluoro-derivatives of aminoacids. Since sulphur tetrafluoride reacts with amino- and carboxy-groups, liquid hydrogen fluoride, which converts the amino-group into the ammonium group $NH_3^{\oplus}$ which is inert to the action of sulphur tetrafluoride, was used as the solvent in this reaction. In order to prevent the fluorination of the carboxy-group to the trifluoromethyl group, the reaction was performed at low temperatures. In the case of β-hydroxy-α-aminoacids, the fluorination must be carried out also at low reactant concentrations in addition to the conditions indicated above. It has been shown for the interaction of sulphur tetrafluoride with serine (LXXIV) that the reaction is complicated by the formation of the sulphenium salt (LXXV). Further reaction of compound (LXXV) leads to the formation of the initial aminoacid and monofluoroalanine (XXXIII) in proportions of 1 : 1.[58] When the reaction is carried out at high dilution, the formation of the product (LXXV) is prevented, which makes it possible to obtain monofluoroalanine (XXXIII) with a very low serine content (the ratio is 99 : 1).



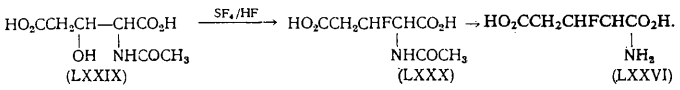
This method, which has been called fluorodehydroxylation, made it possible to obtain 3-fluoro-2-aminobutyric acid (XXXIV)[59] and 3-fluoroaspartic acid (LXXII)[59,60] in moderate yields, apart from monofluoroalanine (XXXIII),[58,59] from the corresponding hydroxy-derivatives.



3-Fluoroglutamic acid (LXXVI) could not be obtained by the fluorodehydroxylation of 3-hydroxyglutamic acid because the lactam (LXXVII) is formed in the fluorination reaction. It was found that acid hydrolysis of compound (LXXVII) takes place only under severe conditions and is accompanied by the elimination of hydrogen fluoride, as a result of which ketoacid (LXXVIII) was isolated as the main reaction product.[61]



The formation of the lactam (LXXVII) can be prevented by using β-hydroxyglutamic acid with a protected amino-group (LXXIX) in the fluorodehydroxylation reaction.

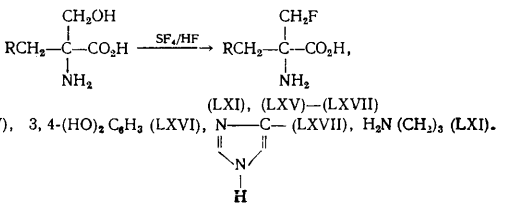


(LXXIX) (LXXX) (LXXVI)

When the acetyl protecting group in compound (LXXX) was removed with the aid of acylase, L-*threo*- and L-*erythro*-isomers of 3-fluoroglutamic acid (LXXVI) were obained in a pure state.[61]

The advantage of the fluorodehydroxylation method is that it is based on readily available initial compounds. Furthermore, optical activity is not lost in the fluorination of pure enantiomers of β-hydroxy-α-aminoacids, since the chiral carbon atom is not involved in the reaction. A disadvantage of the method is the incomplete conversion of the initial aminoacids in many cases, which complicates the isolation of the final products, as well as the formation of fluoro-substituted aminoacids as the hydrofluorides.

The replacement of the hydroxy-group by fluorine in α-hydroxy-derivatives of natural aminoacids with the aid of sulphur tetrafluoride is one of the convenient methods of synthesis of α-(fluoromethyl)-substituted aminoacids, which are irreversible inhibitors of decarboxylases. The initial α-hydroxymethyl derivatives are formed readily on treatment of copper complexes of the corresponding aminoacids with formaldehyde.

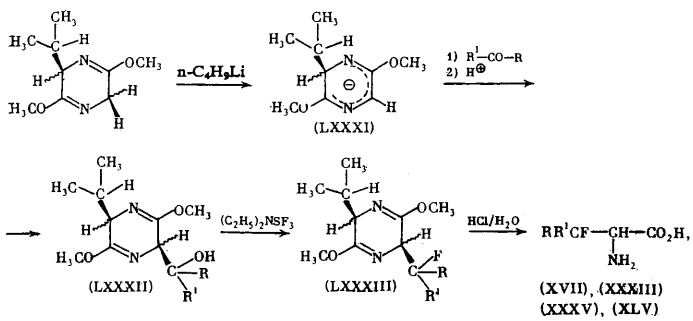


(LXI), (LXV)—(LXVII)

R=4-HOC$_6$H$_4$ (LXV), 3, 4-(HO)$_2$C$_6$H$_3$ (LXVI), N—C— (LXVII), H$_2$N(CH$_2$)$_3$ (LXI).

This method makes it possible to obtain α-fluoromethyl derivatives of aliphatic, aromatic, and heterocyclic aminoacids.[62]

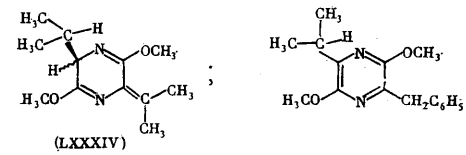
The asymmetric synthesis of certain β-fluoro-substituted aminoacids has been achieved by fluorinating optically active derivatives of dihydropyrazine with diethylaminotrifluorosulphurane $(C_2H_5)_2NSF_3$.[63]



(LXXXI) (LXXXII) (LXXXIII) (XVII), (XXXIII) (XXXV), (XLV)

R = R^1 = H (XXXIII); R = H, R^1 = C$_6$H$_5$ (XVII); R = R^1 = CH$_3$ (XXXV); R = CH$_3$, R^1 = C$_6$H$_5$ (XLV).

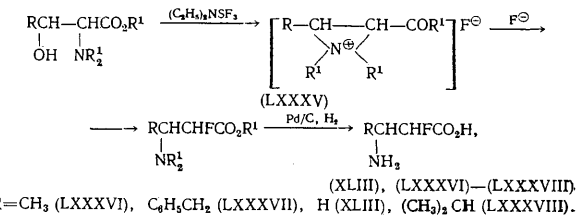
Alkylation of the anion (LXXXI) with carbonyl compounds (acetone, benzaldehyde, acetophenone, formaldehyde) takes place with different optical yields, which are not, however, below 85%. In the case of compound (LXXXII) with R = H and R^1 = C$_6$H$_5$ or R = CH$_3$ and R^1 = C$_6$H$_5$, the ratios of the *erythro*- and *threo*-isomers are 6:1 and 12:1 respectively. Further conversion of the hyroxy-derivatives (LXXXII) into the fluoro-substituted products (LXXXIII) proceeds with moderate yields (~45%) owing to the formation of side products—3-isopropylidenedihydropyrazine (LXXXIV) or a pyrazine derivative.



(LXXXIV)

In compound (LXXXII, R = R^1 = H), the hydroxy-group could not be substituted by the fluoro-group with the aid of diethylamino-trifluorosulphurane (diethylaminosulphur trifluoride, DAST. Ed. of translation). In order to obtain monofluoroalanine, the anion (LXXXI) was therefore made to react with fluoroiodomethane, as a result of which the corresponding monofluoromethyl derivative (LXXXIII, R = R^1 = H) was obtained in 80% yield. The optical yield did not then exceed 45%.

The use of DAST for the fluorination of *NN*-dibenzyl derivatives of β-hydroxy-α-aminoacid esters leads to α-fluoro-β-amino-derivatives.[64]



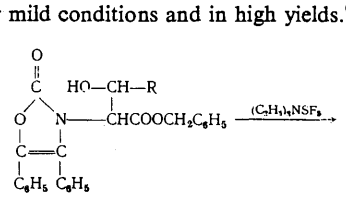
(LXXXV) (XLIII), (LXXXVI)—(LXXXVIII)

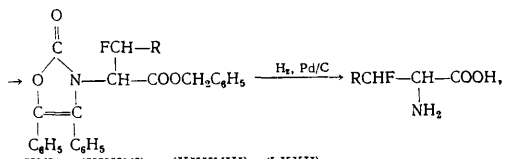
R=CH$_3$ (LXXXVI), C$_6$H$_5$CH$_2$ (LXXXVII), H (XLIII), (CH$_3$)$_2$CH (LXXXVIII).

The formation of β-aminoacids from their α-amino-derivatives is believed[64] to be explained by the intermediate formation of the aziridinium ion (LXXXV), which is attacked by the fluoride anion at the α-carbon atom, affording substituted β-aminoacids in 90% yield. An advantage of this method is its high stereospecificity. Thus the double inversion of the configuration of the α-carbon atom (the formation of the aziridinium ion and the opening of its ring by the fluoride anion) results in the formation from the optically active L- or D-aminoacids of the corresponding optically active α-fluoro-derivatives. Furthermore, in the case of β-hydroxy-α-aminoacids having two asymmetric centres (α- and β-carbon atoms), the initial *erythro*- or *threo*-configuration is retained during their conversion into α-fluoro-β-amino-derivatives.[64]

Free α-fluoro-β-aminoacids (XLIII) and (LXXXVI)—(LXXXVIII) have been obtained by the hydrogenolysis of *NN*-dibenzyl derivatives in the presence of a palladium catalyst.

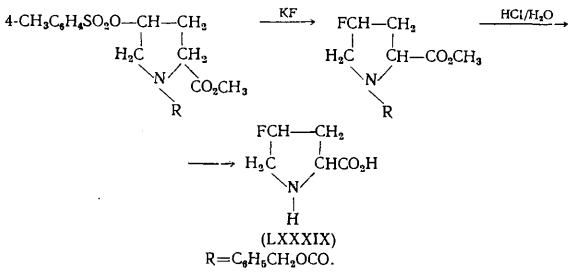
The decrease in the nucleophilicity of the nitrogen atom when the amino-group is protected by employing 4,5-diphenyl-4-oxazolin-2-one rules out the possibility of the isomerisation of α-amino-β-hydroxy-derivatives of carboxylic acid via the aziridinium ion (LXXXV). The employment of DAST in this instance makes it possible to obtain β-fluoro-derivatives of various natural aminoacids under mild conditions and in high yields.[65]





(XVII), (XXXVI) — (XXXVIII), (LXXII)
R=C_6H_5 (XVII), CH_3 (XXXVI), C_2H_5 (XXXVII),
n-C_3H_7 (XXXVIII), COOH (LXXII).

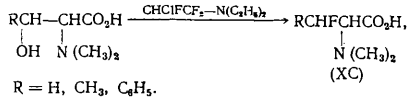
Another method for the substitution of the hydroxy-group by a fluorine atom consists in treatment of *O*-tosyl derivatives of β-hydroxyaminoacid with anhydrous potassium fluoride. This procedure led to the formation of *cis*- and *trans*-4-fluoroprolines (LXXXIX) from hydroxyproline and hydroxyalloproline.[66,67]



(LXXXIX)
R=$C_6H_5CH_2OCO$.

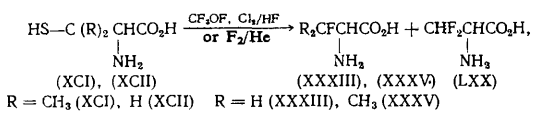
The experiments with *E. coli* have shown that *cis*-4-fluoroproline inhibits protein biosynthesis.

It is noteworthy that the use of 2-chloro-1,1,2-trifluoroethyl-(diethyl)amine (the Yarovenko reagent) as the fluorinating agent for the replacement of the hydroxy-group by fluorine proved to be possible only for aminoacids with a tertiary amino-group. A series of β-fluoro-derivatives of *NN*-dimethylaminoacids (XC) have been obtained by this procedure.[68]



(XC)
R = H, CH_3, C_6H_5.

The synthesis of β-fluoro-substituted aminoacids by the replacement of the mercapto-group by fluorine has been demonstrated in relation to the conversion of D-penicillamine (XCI) into 3-fluoro-D-valine and also by the synthesis of mono- and di-fluoroalanines from 3-mercaptoalanine (XCII).[69]

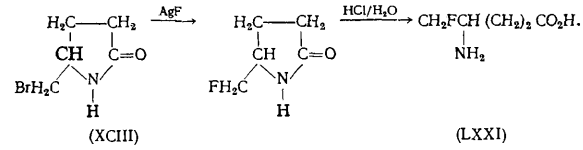


(XCI), (XCII) (XXXIII), (XXXV) (LXX)
R = CH_3 (XCI), H (XCII) R = H (XXXIII), CH_3 (XXXV)

This method, which has been called fluorodesulphurisation,[69] is apparently relatively unsuitable for laboratory practice, since the yields of the final products are low and it requires the employment of trifluoromethyl hypofluorite or elemental fluorine.

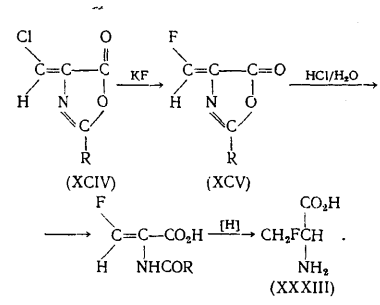
The method of synthesis of fluorinated aminoacids involving the replacement of a halogen atom by fluorine has not found a wide scale application, which is apparently due to the low availability of the initial compounds.

The replacement of a bromine atom in 5-bromomethyl-2-pyrrolidinone (XCIII) by fluorine on treatment with AgF in anhydrous acetonitrile and subsequent acid hydrolysis afforded γ-fluoromethyl-γ-aminobutyric acid (LXXI), which proved to be an effective inactivator of γ-aminobutyric acid transaminase.[70,71]



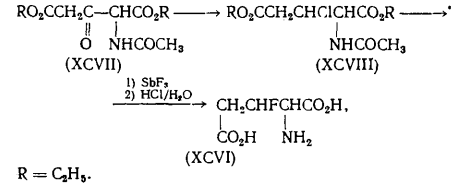
(XCIII) (LXXI)

3-Fluoroalanine (XXXIII) was first obtained by the replacement of the chlorine atom by a fluorine atom on treatment of 4-chloromethylene-2-phenyloxazolinone (XCIV) with potassium fluoride and subsequent hydrolysis and reduction of the fluoro-derivative (XCV).[72]



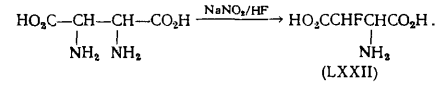
(XCIV) (XCV) (XXXIII)

The employment of antimony trifluoride as the fluorinating agent made it possible to achieve the synthesis of β-fluoroglutamic acid (XCVI) from diethyl 2-acetamidoacetonedicarboxylate (XCVII).[73] The diethyl ester of the ketoacid (XCVII) was reduced and converted by subsequent chlorination into the chloro-derivative (XCVIII), from which the aminoacid (XCVI) was obtained by treatment with antimony trifluoride and subsequent hydrolysis.



(XCVII) (XCVIII) (XCVI)
R = C_2H_5.

A single example of the replacement of the amino-group by a fluorine atom in the synthesis of β-fluoroaspartic acid (LXXII) by the diazotisation of diaminosuccinic acid by treatment with sodium nitrite in liquid hydrogen fluoride is known.[74] By carrying out the reaction at a reduced temperature, it is possible to replace selectively only one amino-group by fluorine.



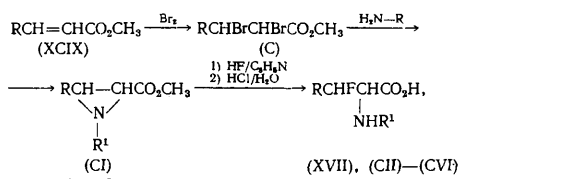
(LXXII)

2. Syntheses based on the opening of the rings of fluorine-containing heterocyclic compounds

The majority of methods considered in this section are feasible because of the specific effect of fluorine atoms or perfluoroalkyl groups. In the case of non-fluorinated compounds, these reactions are inapplicable or lead to other products. Syntheses of this type give rise to the possibility of obtaining individual β-fluoro-derivatives of aminoacids, but in many instances the approaches are general and can be used to synthesise a series of fluorinated aminoacids.

The procedure based on the opening of the aziridine[75–79] or azirine[80] ring by the Olah reagent ($HF.C_5H_5N$) can be regarded as one of the most modern and general methods of synthesis of β-fluoro-derivatives of aminoacids (mono- and difluorinated).

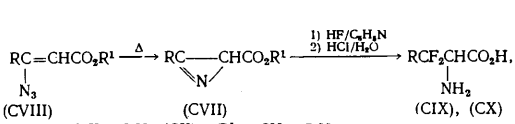
The starting materials for the synthesis of monofluoro-compounds were substituted acrylic esters (XCIX), which were converted by bromination into the dibromo-derivatives (C) and the aziridines (CI) were obtained by subsequent treatment with ammonia. The aziridines afford the corresponding aminoacids in high yields on treatment with the Olah reagent. The use of alkylamines instead of ammonia in this reaction permits the synthesis of *N*-substituted derivatives of fluorinated aminoacids.



(XCIX) (C) (CI) (XVII), (CII)—(CVI)

R = H, $R^1 = (CH_3)_3C$ (CII); R = $R^1 = CH_3$ (CIII); R = C_6H_5, R^1 = H (XVII); R = C_6H_5, $R^1 = CH_3$ (CIV); R = 4-ClC_6H_4, R^1 = H (CV); R = 4-ClC_6H_4, $R^1 = CH_3$ (CVI).

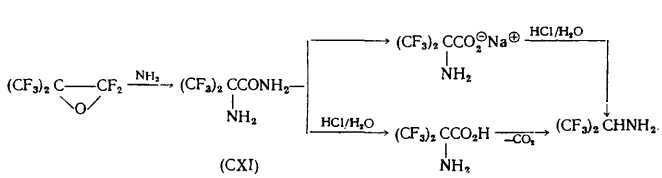
Treatment with the Olah reagent of the azirinecarboxylates (CVII), formed on thermal decomposition of the azides (CVIII), is a convenient method of synthesis of ββ-difluoro-derivatives of aminoacids (yield 37–42%).



(CVIII) (CVII) (CIX), (CX)

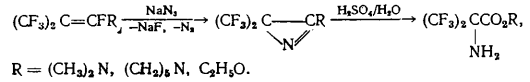
R = CH_3 (CIX), C_6H_5 (CX); $R^1 = CH_3$, C_2H_5.

The opening of the three-membered oxiran and azirine rings containing perfluoroalkyl groups has also been used to synthesise β-fluoro-derivatives of aminoacids. Thus interaction of perfluoroisobutene oxide with ammonia[81] affords the amide of 3,3,3,3′,3′,3′-hexafluoro-2-aminoisobutyric acid (CXI). The attempt to hydrolyse the amide (CXI) with dilute hydrochloric acid causes the decarboxylation of the aminoacid with formation of hexafluoroisopropylamine. Nevertheless, by means of alkaline hydrolysis it has been possible to isolate the sodium salt of hexafluoro-2-aminoisobutyric acid, which, however, also decarboxylates on acidification.[82]



(CXI)

Other derivatives of hexafluoro-α-aminoisobutyric acid—dialkylamides and the ethyl ester—were obtained by the hydrolysis of the corresponding azirines, which are formed readily on treatment of dialkylamino- or ethoxy-derivatives of perfluoroisobutene with sodium azide.[83,84]

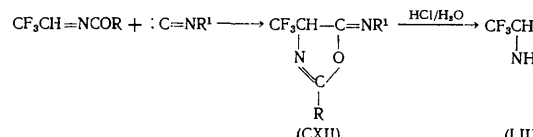


R = $(CH_3)_2N$, $(CH_2)_5N$, C_2H_5O.

It is noteworthy that derivatives of hexafluoro-α-aminoisobutyric acid do not form stable salts even with H_2SO_4, which has been explained by the electron-accepting influence of the two trifluoromethyl groups in the α-position relative to the amino-group.

A series of methods based on the formation and opening of the oxazole ring have been proposed for the synthesis of 3,3,3-trifluoroalanine. A disadvantage of these methods is their multistage nature, which reduces appreciably the yield of the product.

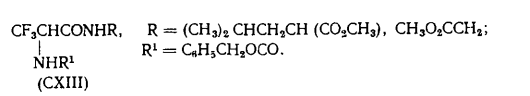
Trifluoroalanine (LIII) was first obtained by the acid hydrolysis of the oxazolines (CXII) formed on [1 + 4]cycloaddition of *N*-acyltrifluoroacetaldimines to isonitriles.[85]



(CXII) (LIII)

R = $C_6H_5CH_2O$; $R^1 = n\text{-}C_6H_{11}$.

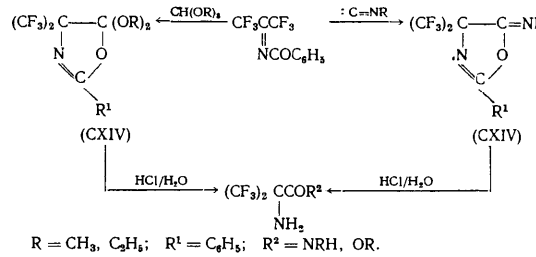
The use in this reaction of isonitriles synthesised from *N*-formylaminoacid esters made it possible to obtain trifluoroalanyl peptides (CXIII).[85]



(CXIII)

It is noteworthy that alkaline hydrolysis of alanine derivatives (LIII) takes place with conversion of the trifluoromethyl group into the carboxy-group.

Like *N*-acyltrifluoroacetaldimines, hexafluoroacetone *N*-benzoylimine readily enters into the [1 + 4]cycloaddition reaction with isonitriles and orthoformic ester. Hydrolysis of the oxazolines (CXIV) formed affords derivatives of the unstable 3,3,3,3′3′,3′-hexafluoro-2-aminoisobutyric acid.[86,87]

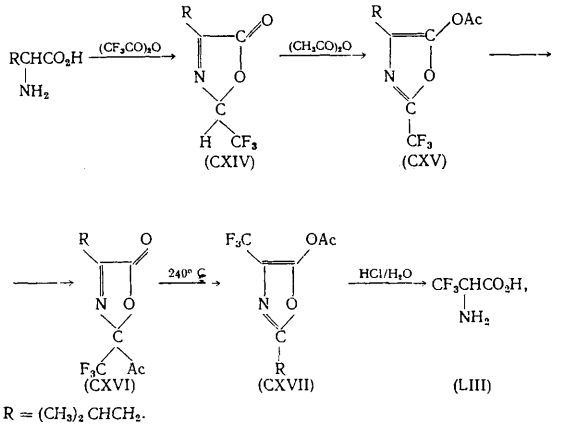


(CXIV) (CXIV)

R = CH_3, C_2H_5; $R^1 = C_6H_5$; R^2 = NRH, OR.

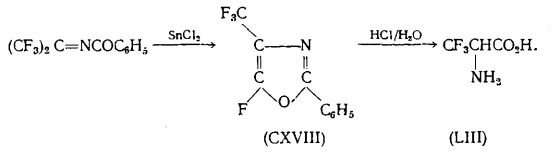
Another approach to the synthesis of trifluoroalanine (LIII) involves the cyclisation of *N*-trifluoroacetyl derivatives of aminoacids to the oxazolines (CXIV), their subsequent conversion into the oxazoles (CXV), and the isomerisation of the latter by treatment with γ-(*NN*-dimethylamino)pyridine to the oxazolines (CXVI), whose

brief heating at 240 °C affords the oxazoles (CXVII). Acid hydrolysis of the latter yields trifluoroalanine (LIII).[88,89]

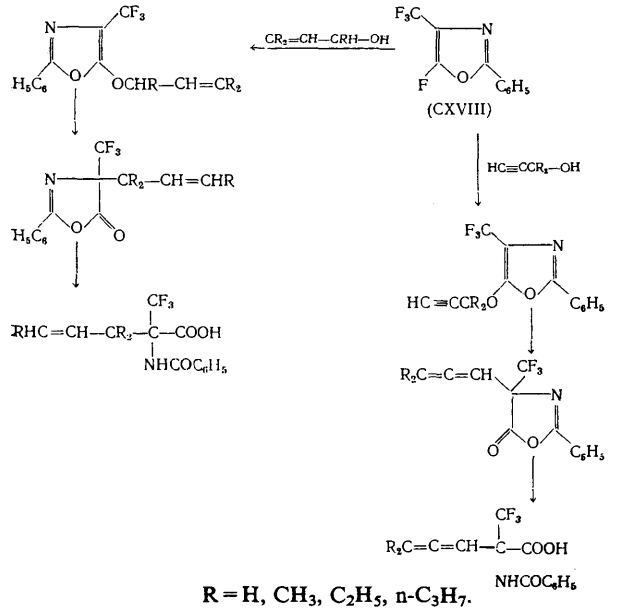


R = $(CH_3)_2CHCH_2$.

An interesting method of synthesis of trifluoroalanines (LIII) from hexafluoroacetone benzoylamine has been proposed.[90] It was found that hexafluoroacetone *N*-benzoylamine cyclises on treatment with tin dichloride to the oxazole (CXVIII) whose hydrolysis affords trifluoroalanine (LIII) in a overall 20% yield.

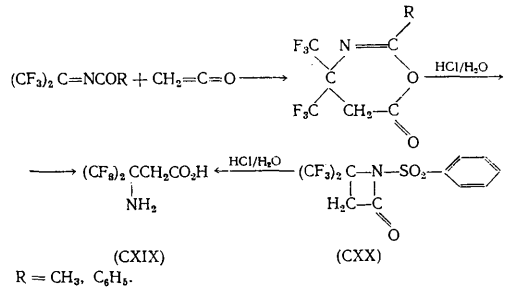


The possibility of substituting the fluorine atom in the 5-position of the oxazole ring of compound (CXVIII) in reactions with alcohols has been used successfully in devising a general method of synthesis of novel compounds—2-allyl- and 2-allenyl-3,3,3-trifluoroalanines.[91]



R = H, CH_3, C_2H_5, n-C_3H_7.

The introduction of hexafluoroacetone N-acylimines into the [4+2]cycloaddition reaction with the keten and subsequent hydrolysis of the resulting oxazinones leads to β-amino-ββ-bis-(trifluoromethyl)propionic acid (CXIX).[87]

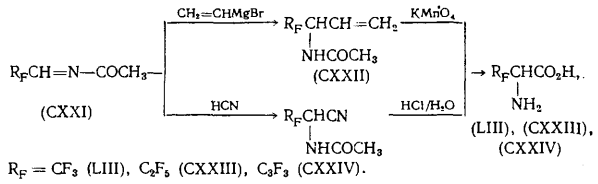


R = CH_3, C_6H_5.

The β-alanine derivative (CXIX) has also been obtained by the reaction of keten with hexafluoroacetone *N*-toluene-*p*-sulphonylimine and subsequent hydrolysis of the propiolactam (CXX).[92]

3. Synthesis of α-perfluoroalkylaminoacids from the *N*-acylimines of fluorinated aldehydes and ketoacids

A general method of synthesis of α-perfluoroalkylglycines from the *N*-acylimines of perfluorinated aldehydes (CXXI) has been developed.[85,93–96] Vinylmagnesium bromide adds readily to the C=N bond of the azomethines (CXXI) with formation of the derivatives (CXXII). Oxidation of the C=C bond in compounds (CXXII) with potassium permanganate and subsequent hydrolysis leads to the α-perfluoroalkyl-substituted aminoacids (LIII), CXXIII), and (CXXIV). The possibility of synthesising such aminoacids by adding hydrocyanic acid to the acylimines (CXXI) and the hydrolysis of the resulting nitriles has been demonstrated.



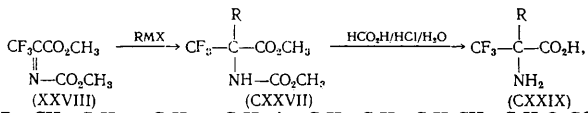
R_F = CF_3 (LIII), C_2F_5 (CXXIII), C_3F_3 (CXXIV).

The sulphone (CXXV) or the halogeno-derivatives (CXXVI) can be used as species equivalent to the imines (CXXI) in the above reaction, but the presence of a base (triethylamine) is then essential.



Trifluoroalanine (LIII) has also been obtained by substituting the chlorine atom by the CN group on treatment of the chloro-derivative (CXXVI) with CuCN[97] and subsequent hydrolysis of the corresponding cyanamide.

A method based on the alkylation of the *N*-methoxycarbonylimine of methyl trifluoropyruvate (XXVIII) for the synthesis of β-fluoro-substituted aminoacids which are most difficult to obtain, namely α-trifluoromethylaminoacids, has been proposed recently.[98,99]

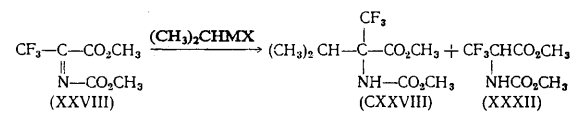


(XXVIII) (CXXVII) (CXXIX)

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, C_6H_5, $C_6H_5CH_2$, $C_2H_5O_2CCH_2$;
M = Mg, Zn, Cd; X = Cl, Br, I.

The regioselective alkylation of the *N*-methylcarbonylimine (XXVIII) with organomagnesium compounds can be achieved only by mixing the reactants at the liquid nitrogen temperature with subsequent heating of the reaction mixture at 20 °C because of the high electrophilicity of the imine (XXVIII). The use of less reactive organocadmium compounds permits the alkylation of the imine (XXVIII) at 4 °C. The yields of the aminoesters (CXXVII) are almost independent of the metal employed and amount to 60–90%.

In the synthesis of α-trifluoromethylvaline by alkylating the *N*-methoxycarbonylimine (XXVIII) with diisopropylcadmium or isopropylmagnesium bromide, the reaction is complicated by the reduction of the imine (XXVIII) to the methyl ester of *N*-methoxycarbonyl-3,3,3-trifluoroalanine (XXVII).[100]



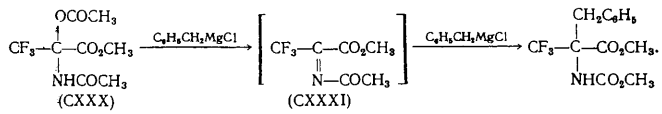
(XXVIII) (CXXVIII) (XXXII)

M = Mg, X = Br; MX = CdCH $(CH_3)_2$.

In the case of isopropylmagnesium bromide, the ratio of compounds (CXXVIII) and (XXXII) is 1.5:1, while the use of diisopropylcadmium makes it possible to obtain predominantly the valine derivative (CXXVIII).

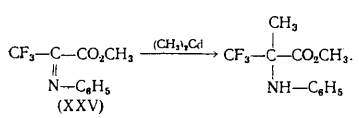
The amidoesters (CXXVII) and (CXXVIII) proved to be resistant to acid hydrolysis. In order to obtain the hydrochlorides of α-trifluoromethylaminoacids (CXXIX), it is essential to heat compounds (CXXVII) and (CXXVIII) in a mixture of concentrated hydrochloric and formic acids at 100 °C for 40 h.

The possibility of synthesising α-trifluoromethylaminoacids by treating with two moles of an organomagnesium reagent the diacetyl derivative (CXXX), which can be regarded as a species equivalent to the *N*-acetylimine (CXXXI), has been demonstrated.[99]



(CXXX) (CXXXI)

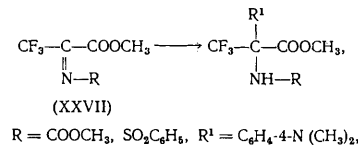
The use of the *N*-alkylimines of methyl trifluoropyruvate in reactions with organometallic reagents in order to synthesise *N*-alkyl-substituted α-trifluoromethylaminoacids proved unsuccessful. However, the *N*-phenylimine (XXV) was alkylated with dimethylcadmium to form the methyl ester of *N*-phenyl-α-trifluoromethylalanine.[99]



(XXV)

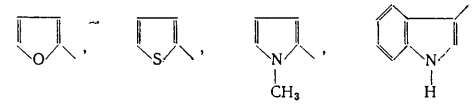
An advantage of the method considered is the availability of the reagents employed and also the high yields of α-trifluoromethylaminoacids. However, its disadvantage is that its application in the synthesis of heterocyclic or polyfunctional natural aminoacids is problematical.

One of the prospects for the further application of imines of methyl trifluoropyruvate in the synthesis of α-trifluoromethyl-substituted aminoacids apparently involves the use of these compounds in *C*-alkylation and cycloaddition reactions. Thus the high electrophilicity of the *N*-acylimines (XXVII) makes it possible to synthesise derivatives of 2-aryl- and 2-heteroaryl-3,3,3-trifluoroalanines by the regioselective alkylation of *NN*-dimethylalanine and a series of heterocycles.[101,102]

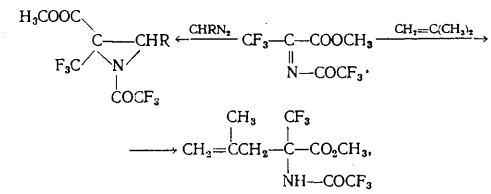


(XXVII)

R = $COOCH_3$, $SO_2C_6H_5$, R^1 = C_6H_4-4-N $(CH_3)_2$,



Furthermore, the introduction of the *N*-trifluoroacetylimine of methyl trifluoropyruvate into the reaction with diazo-compounds and alkenes made it possible to obtain derivatives of α-trifluoromethylcoronamic acid and α-trifluoromethyl-γδ-dehydroleucine.[103]



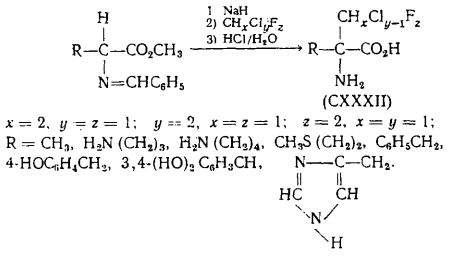
R = H, $COOC_2H_5$.

4. Halogenoalkylation of the α-C-anions of protected aminoacids

A method involving the fluoromethylation of the α-C-anions of protected aminoacids has been developed comparatively recently for the synthesis of α-monofluoromethyl- and α-difluoromethyl-substituted aminoacids.

The carboxy-group in the initial aminoacids was protected by conversion into the methyl ester and the amino-group was protected by conversion into a Schiff base by treatment with benzaldehyde. In those cases where the aminoacid molecules contained OH and SH groups, the latter were converted into ether and sulphide groups; in order to protect the NH groups, for example, in histidine, the *N*-trityl derivative was obtained. The α-C-anions of aminoacids protected in this way were obtained by employing strong bases such as lithium diisopropylamide, sodium hydride, and potassium t-butoxide. The aminoacid C-anions proved to be most stable in tetrahydrofuran (for 24 h), which was used as the solvent. The subsequent alkylation of the C-anions with chlorofluoro- or chlorodifluoro-methane leads to the formation of the α-monofluoroethyl or α-difloromethyl derivatives of aminoacids (CXXXII) after the removal of the protecting group.[45,104,105] The use of the Freon

$CHCl_2F$ makes it possible to obtain the corresponding α-chlorofluoromethyl derivatives. The latter proved to be less stable than the difluoromethyl-substituted aminoacid.



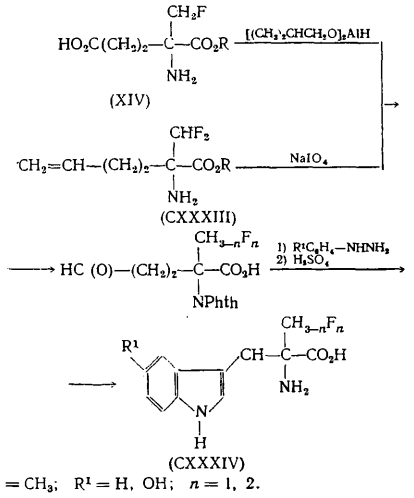
(CXXXII)

$x = 2$, $y = z = 1$; $y = 2$, $x = z = 1$; $z = 2$, $x = y = 1$;
$R = CH_3$, $H_2N(CH_2)_3$, $H_2N(CH_2)_4$, $CH_3S(CH_2)_2$, $C_6H_5CH_2$, 4-$HOC_6H_4CH_2$, 3,4-$(HO)_2C_6H_3CH$,

This method proved to be applicable to both aliphatic and aromatic and to heterocyclic and polyfunctional aminoacids. The yields of the fluorinated aminoacids are 20–50%.

The formation of a dihalogenocarbene on halogenoalkylation[104] of aminoacid Schiff bases precludes the formation of α-trifluoromethyl derivatives of aminoacids by this reaction using chlorotrifluoromethane or bromotrifluoromethane.

The possibility of the introduction of further functional groups into fluorine-containing aminoacids greatly extends the limits of the applicability of known methods. Thus α-fluoromethylglutamic acid (XIV) and 2-butenyl-3,3-difluoroalanine (CXXXIII), obtained by the halogenoalkylation of the corresponding Schiff bases of the methyl esters of the aminoacids, were used as the starting compounds in the synthesis of α-monofluoromethyl- and α-difluoromethyl-tryptophans and their 5-hydroxy-derivatives (CXXXIV) in accordance with the following scheme:[106]



(XIV)

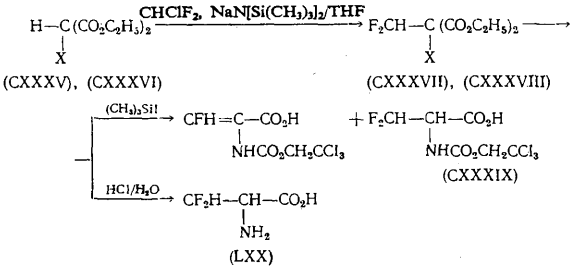
(CXXXIII)

(CXXXIV)

$R = CH_3$; $R^1 = H$, OH; $n = 1$, 2.

α-Monofluoromethyl- and α-difluoromethyl-tryptophans (CXXXIV) proved to be inhibitors of aromatic aminoacid decarboxylases.[106]

It is noteworthy that monofluoro- or difluoro-alanine could not be obtained directly from protected glycine. Therefore, *N*-substituted derivatives of aminomalonic ester (CXXXV) were used as the initial compounds for the synthesis of difluoroalanine (LXX).[107,108] The C-anions were obtained from compounds (CXXXV) in tetrahydrofuran using sodium hexamethyldisilazanide as the base. Subsequent alkylation of the C-anions obtained in this way with chlorodifluoromethane leads to the formation of the difluoromethyl derivatives (CXXXVII) in a yield which is high for reactions of this type (50%).



(CXXXV), (CXXXVI) (CXXXVII), (CXXXVIII)

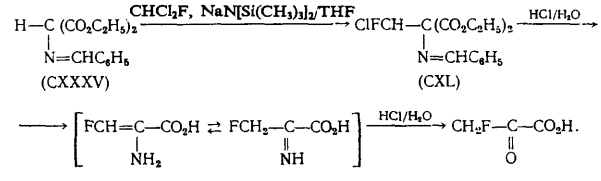
(CXXXIX)

(LXX)

$X = N{=}CHC_6H_5$ (CXXXV), (CXXXVII); $NHCO_2CH_2CCl_3$ (CXXXVI), (CXXXVIII).

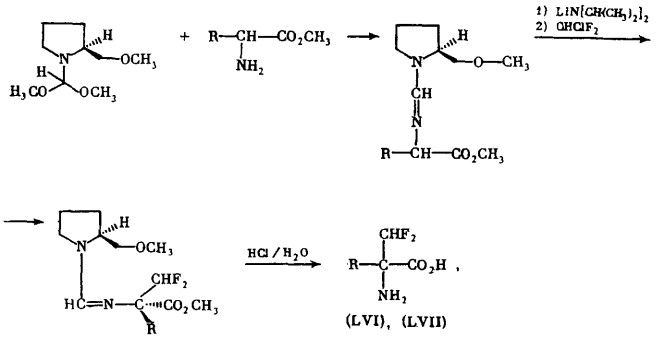
The hydrolysis and decarboxylation of the Schiff base (CXXXVII) take place readily with formation of difluoroalanine (LXX), while the carbamate (CXXXVIII) proved to be extremely resistant to acid hydrolysis. Alkaline hydrolysis proved to be inapplicable in the given instance in view of dehydrofluorination. The employment of trimethylsilyl iodide made it possible to remove only the ester group with formation of the acid (CXXXIX). Together with compound (CXXXIX), the product of the dehydrofluorination of the urethane (CXXXVIII), namely *N*-acyl-β-fluorodehydroalanine, was detected in this reaction.

The use of dichlorofluoromethane for the alkylation of the C-anion obtained from the Schiff base (CXXXV) permitted the synthesis of the chlorofluoromethyl derivative (CXL). However, the corresponding β-chloro-β-fluoroalanine could not be isolated because of the lack of resistance of compound (CXL) even to acid hydrolysis. The main reaction product proved to be monofluoropyruvic acid formed in accordance with the scheme[107]



(CXXXV) (CXL)

The employment of (*S*)-(−)-1-dimethoxymethyl-2-methoxymethylpyrrolidine to protect the amino-group made it possible to achieve the asymmetric synthesis of α-difluoromethyl-substituted alanine (LXI) and phenylalanine (LVII).[109,110]



(LVI), (LVII)

$R = CH_3$ (LVI), $C_6H_5CH_2$ (LVII).

IV. Conclusion

The literature data examined show that the methods of synthesis of β-fluoro-substituted aminoacids available at present permit the preparation of almost all possible types of these compounds containing between one and three fluorine atoms in the β-position relative to the amino-group. Nevertheless, the impressive results of studies on the biological properties of fluorine-containing aminoacids have stimulated the search for new more convenient methods of synthesis of these compounds.

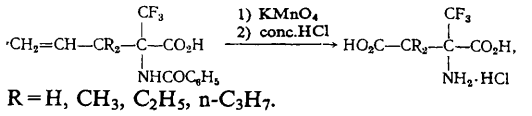
Together with advances in the synthesis of β-fluoro-substituted aminoacids, there still exist problems for which optimum solutions have not been found. This applies particularly to polyfunctional and optically active compounds.

It is to be expected that further studies on the synthesis of β-fluoro-substituted aminoacids will be directed in the first place mainly towards the creation of new simpler and more convenient methods of synthesis of known as well as still unknown representatives of the series of β-fluoro-derivatives of aminoacids and secondly, they will be directed towards the development of an asymmetric synthesis of these compounds, which will permit a more detailed investigation of the biological activity of β-fluoro-substituted aminoacids and also their use in the synthesis of peptides.

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During the preparation of the review for the press, several new studies illustrating further utilisation of the synthetic possibilities of the methods described above for the preparation of α-trifluoromethyl-α-aminoacids were published.

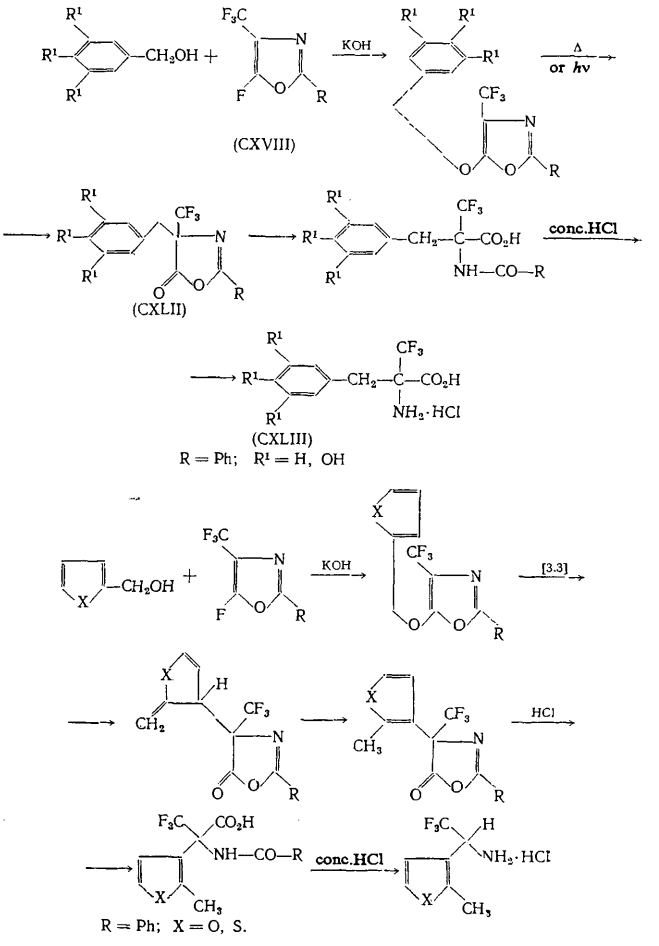
α-Trifluoromethylaspartic acid as well as its previously unknown 3-alkyl- and 3,3-dialkyl-derivatives were obtained by oxidising the C=C double bond in 2-allyltrifluoroalanines (CXLI), synthesised from 5-fluoro-4-trifluoromethyloxazole (CXVIII) and the corresponding allyl alcohols.[111]



R = H, CH_3, C_2H_5, n-C_3H_7.

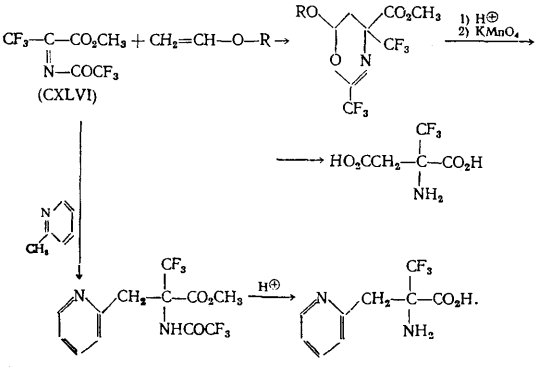
A series of 4-benzyl-4-trifluoromethyl-5(4*H*)-oxazolones (CXLII) were synthesised by the reaction of benzyl alcohols (the allyl double bond is a purely aromatic system) with 5-fluoro-4-fluoromethyloxazole (CXVIII) and subsequent rearrangement of the resulting products. The hydrolysis of the oxazolones affords α-trifluoromethylphenylalanines (CXLIII).[112]

The use of 2-hydroxymethyl-substituted furan and thiophene in the analogous reactions with oxazole (CXVIII) is limited to the formation of only *N*-acyl derivatives of 3-heteroaryltrifluoroalanines (CXLIV). This is associated with the fact that under the conditions corresponding to the removal of the *N*-protecting group (refluxing in concentrated HCl), decarboxylation takes place readily with formation of the corresponding amines (CXLV).[112]



Yet another general approach to the synthesis of α-trifluoromethyl-α-aminoacids, based on the reactions of the *N*-acylimines of methyl trifluoropyruvate has also been developed further.

The introduction of *N*-trifluoroacetylimine (CXLVI) into the [4+2]cycloaddition reaction with vinyl ethers and the subsequent hydrolysis and oxidation reactions of the product constitute yet another convenient method of synthesis of α-trifluoromethylaspartic acid.[113]



The regioselective *C*-alkylation of 2-methylpyridine with the *N*-trifluoroacetylimine (CXLVI) is of special interest.[114] This reaction opens a pathway to the synthesis of the virtually uninvestigated β-heteroaryl-α-trifluoromethylalanines.

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Laser-induced chemical deposition from the gas phase

V V Teslenko

ABSTRACT. The results of the study of the chemical reactions involved in the deposition of various substances from the gas phase using the pulsed, quasi-continuous, and continuous laser radiation in the wavelength range 0.193–10.6 μm have been summarised. Particular attention has been paid to the deposition of inorganic substances, including non-metals (C, Si, Ge, etc.), metals (Cu, Au, Zn, Cd, Al, Cr, Mo, W, Ni), and a number of simple compounds. Detailed experimental data are given on the influence of the radiation parameters (wavelength, duration and spacing of the pulses, intensity of radiation, shape and position of the laser beam) and the nature of the reagents (hydrides, halides, carbonyls, alkyl organometallic compounds, etc.) on the rate of deposition and the composition of the deposit. The characteristics of photolytic deposition reactions and their possible applications have been examined.

The bibliography contains 202 references.

Contents

I.	Introduction	103
II.	Deposition of non-metals	103
III.	Deposition of metals	106
IV.	Deposition of inorganic compounds	109
V.	Characteristics of laser-induced chemical deposition reactions	111
VI.	Possible applications of laser-induced deposition processes	112
VII.	Summary	112

I. Introduction

Reactions involving chemical deposition from the gas phase are finding extensive practical application. In addition to the traditional method in which the reagents are heated, the attention of chemists in recent years has been drawn to other methods of initiating chemical reactions, such as plasma excitation and laser irradiation.

The first paper on the chemical deposition of carbon induced by the radiation of a CO_2 laser appeared in 1972.[1] In the period up to 1980, not more than ten papers on this topic[2–9] were published, but by 1988 the number of papers, reports, and patents exceeded 200. Most of the credit for this goes to specialists in electronics, who not only carried out a large number of studies but also published a whole series of reviews,[10–18] although these are short and highly specialised.

The chemical processes of deposition from the gas phase induced by laser radiation have a wider practical importance, however.[19–24] They can be regarded as a new field of laser chemistry, adjoining, for example, the field of gas-phase laser chemistry.[25–27] This has made it appropriate to publish the present review, which has the following aims: 1) to summarise the experimental data for the period 1980–1987; 2) to describe the principal characteristics of laser-induced chemical deposition reactions; and 3) to examine the possible applications of the process.

The possibility of laser-induced chemical deposition reactions was studied in detail by a number of authors.[8,16,23,28] Here it is sufficient to note that this method can apparently be used to bring about all reactions of chemical deposition from the gas phase (a list of reactions has been published[29–31]), and also a number of other reactions, in particular the decomposition of transition metal halides, such as $TiCl_4$.[32] Two main types of reaction are distinguished, depending on the nature of the interaction of the laser-radiation with the substance: 1) laser-chemical reactions, in which the electromagnetic energy is used up only in the rupture of bonds in the starting materials, and is not converted into thermal energy; and 2) laser-thermal reactions, in which the reagent is first heated, and then undergoes thermochemical transformation. In the English-language literature, these reaction types are described as photolytic and pyrolytic respectively.

The minimum size of the reaction zone is comparable with the wavelength of the radiation; the value attainable in practice is 0.5 μm for photolytic processes, and several μm for pyrolytic processes.[33] Assemblies for carrying out laser-induced deposition are of three main types: in the first type, the laser radiation interacts with a gas in a free space (power synthesis),[34] in the second it interacts close to the surface of a support (deposition of amorphous and microcrystalline coatings),[35–38] and in the third it interacts when the beam reaches the surface of the support (formation of point deposits and non-planar bands, growth of rods, preparation of polycrystalline coatings).[39–41] In addition, there are combined assemblies, for example assemblies using crossed beams.[42–49] The most frequently used are assemblies with the perpendicular configuration, in which the laser beam is directed on to the support, and assemblies with the parallel configuration, in which a beam with a circular or rectangular cross-section is passed several millimetres above the surface of a planar support.

II. Deposition of non-metals

Carbon is obtained by the pyrolysis of hydrocarbons.[1,3,50–56] The production of spiral bands with a width of 0.35 mm on a ceramic rod with a diameter of 3.5 mm by irradiating it in a hydrocarbon atmosphere with a CO_2 laser has been described.[3] The same radiation with metallic supports was used to grow fibrous graphite crystals with a diameter of less than 1 μm and diamond-like films.[50,51] The technical assembly "Kvant-12" has been used to obtain films with a thickness of up to 40 μm on a metal or ceramic support.[52] The decomposition of acetone vapour by heating glass, mica, and crystalline glass supports by radiation with a power of up to 1 W and wavelength λ = 0.53 um (diameter of the focal spot

50 μm) made it possible to obtain rods of polycrystalline graphite with a diameter of 40 μm and a length of up to 3 mm; except for the initial period, the rate of growth (70–230 μm min^{-1}) was proportional to the radiation power.[56] The deposition of carbon from C_2H_2, C_2H_4, and CH_4 on graphite, tungsten, and aluminium oxide supports heated by the radiation of an Ar^+ laser has been described.[53,54] The deposit was obtained in two forms. When the laser beam scanned the surface of the support at a rate of 42 μm s^{-1}, non-planar polycrystalline bands with widths of 5–26 μm were deposited. Stationary irradiation of the support gave cylindrical carbon rods with a diameter of 10–70 μm and a length of up to 1 mm. The volume rate of deposition of carbon from acetylene increased non-linearly with increase in the intensity of the irradiation (I); no deposition was detected at I < 54 kW cm^{-2}, and at I > 292 kW cm^{-2}, homogeneous deposition took place close to the surface of the support to give flakes of carbon black. The range of values of I in which heterogeneous deposition of carbon was observed with C_2H_4 and CH_4 were used was greater, and corresponded to 82–760 kW cm^{-2} and 1055–2190 kW cm^{-2} respectively.[53] The measured axial rates of growth of the carbon rod at different temperatures and pressures are given in Fig. 1. The rate of deposition in the temperature range 1500–2500 °C at partial pressures $p_{C_2H_2}$ in the range 6.7–98 kPa had values in the range 0.2–35 μm s^{-1}; up to 2000 °C, the activation energy was 200 kJ mol^{-1}, and the order of the reaction with respect to C_2H_2 was close to 1. Above 2200 °C, the activation energy decreased, apparently indicating that the process moves from the kinetic into the diffusion range.[54] All the processes described were pyrolytic.

The photolytic decomposition of C_2H_4 under the influence of a CO_2 laser (pulse energy E = 0.7 J) at a pressure of 665 Pa has been carried out on an assembly with the parallel configuration.[55] A carbon layer with an area of 5 mm^2 and a thickness of 0.1 μm was deposited on an NaCl support at a distance of 1 mm from the focus (dose D = 300 J cm^{-2}) after pulse irradiation with 50 000 pulses. The carbon had an amorphous structure with the inclusion of individual crystallites of carbyne and lamellar graphite. In the pulse irradiation of ethylene, thermal equilibrium was not established, so that unstable phases were deposited.

High-intensity ultraviolet radiation brings about the formation of a plasma, from which carbon-containing radicals and ions may diffuse to the surface of a support situated 2–3 mm from the focus, and react on it to give carbon. Thus focussing radiation with λ = 308 nm and a power W = 5 MW with a pulse duration τ = 7.5 ns and a pulse repetition frequency ν = 5 Hz gave an intensity of radiation I = 10^5 kW cm^{-2}.[55] On passage through the laser plasma, naphthalene vapour decomposed, and carbon was deposited on the support (polished SiO_2) as a diamond-like coating with a thickness of about 1 μm. The degree of transformation (and rate of deposition) increased when a magnetic or electric field was used,[40,55] as a result of the increase in the rate of the transport of the active species from the generation zone to the surface of the support.

The largest number of papers has been devoted to the deposition of silicon,[5,7,38,42–44,46,48,54,57–83] indicating the considerable practical interest in this process.

When assemblies with the perpendicular configuration were used, the support was heated by the radiation to 900–1400 °C, so that the deposit had a crystalline structure. Silicon is often deposited using a CO_2 laser,[57,59,69,73] and SiH_4 or a mixture of $SiCl_4$ and H_2 as the reagent.[59] In the last study, polycrystalline coatings with a particle size of 8 μm were obtained at a temperature of the quartz support equal to 900 °C (W = 18.9 W). The rate of deposition v was 5.1 μm min^{-1}, and increased with increase in temperature; saturation took place at a radiation power W = 20 W. The activation energy of the process E_a = 154 kJ mol^{-1}. When the support is heated by the radiation of an Ar^+ laser[74] to 1400 K (at p_{SiH_4} = 13.3 kPa), the temperature dependence of the rate of deposition of polycrystalline silicon is described by an Arrhenius equation with E_a = 195 kJ mol^{-1}. The characteristic deviation of the experimental points from the Arrhenius straight line at temperatures above 1400 K indicates that the process moves from the kinetic into the diffusion range. Under these conditions, the process remains in the kinetic range to a higher temperature than in the ordinary pyrolysis of SiH_4.

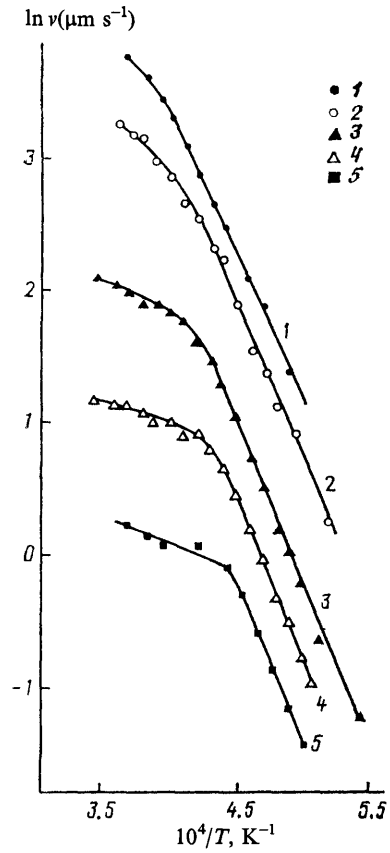


Figure 1. Temperature dependence of the rate of deposition of carbon from C_2H_2 at different partial pressures, kPa: *1*, 98.0, *2*, 66.5, *3*, 26.6, *4*, 13.3, *5*, 6.7.[54]

Single crystals of Si have been deposited using laser radiation with a wavelength of 530.9 nm.[63] Faceted rods with a length of several millimetres and a diameter of about 0.1 mm have been grown on silicon supports with the (100), (110), (111) orientation at 1650 K and p_{SiH_4} = 13.3 kPa at a rate of 30 μm s^{-1}. The axes of the rods coincided with the [100] or [110] directions, irrespective of the orientation of the support. The profile of the growing end of the rod resembled a parabola. Silane and a laser beam with a diameter d = 22 μm were used in the experiments. At deposition temperatures of 1450 K and 1550 K the rods were polycrystalline.

The dependence of the rate of deposition and structure of silicon on the angle of incidence of the radiation, I, p_{SiH_4}, and the temperature of the support (T_s) has been studied.[43,71] With decrease in the angle of incidence from 90° to 0°, the structure of the deposit changed from polycrystalline to amorphous,[71] and the deposition was quenched at a low radiation intensity.[43]

The production of films of amorphous hydrogenated silicon (*a*-Si:H) on assemblies with the parallel configuration is based on the excitation and dissociation of SiH_4 molecules, which show strong resonance absorption at certain wavenumbers in the infrared range (mainly 913.3 cm^{-1}). Mass-spectrometric measurements showed that the action of the laser beam increases the concentration of H_2 and SiH_n^+ (n = 0–4); $Si_2H_n^+$ (n = 1–7) peaks were also observed, indicating the formation of disilane as a result of the high density of radicals in the irradiated volume.[65,66]

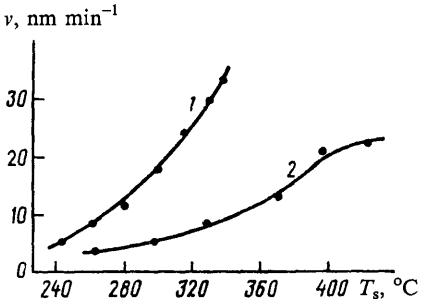


Figure 2. Temperature dependence of the rate of deposition of amorphous silicon at I = 250 W cm^{-2}: *1*, p_{SiH_4} = 0.57 kPa, p_{tot} = 1.33 kPa, gas consumption 5.75 cm^3 s^{-1}; *2*, p_{SiH_4} = 0.43 kPa, p_{tot} = 1.05 kPa, gas consumption 4.25 cm^3 s^{-1}.[57]

Although dissociation in the gas phase takes place even at room temperature, an appreciable rate of heterogeneous deposition is achieved only on a support heated above 200 °C. Fig. 2 gives data on the temperature dependence of the rate of deposition of silicon.[57] The maximum rate of deposition is limited on the one hand by the formation of a powder, and on the other hand by the decrease in the silane concentration as it is used up. The diameter of the laser beam d and the distance from the support are also important. Thus at T_s = 310 °C and W = 65–80 W, the rate of deposition at d = 7.5 mm is approximately twice that at d = 4.0 mm. The explanation for this unexpected result was that in a narrow beam, the degree of dissociation rapidly reaches a limiting value with increase in I, whereas in a broad beam, a larger number of reagent molecules are involved in the process.

The concentration of hydrogen in the deposit and the nature of the bonds it forms with silicon depend markedly on T_s. The infrared spectra showed that films with a thickness of 1 μm contained SiH_2 and SiH groups. Heating at 350–450 °C led to a decrease in the hydrogen concentration (mainly as a result of the decomposition of SiH_2), and heating at 550–650 °C led to crystallisation of the deposit.

Similar results were obtained[64,68–70] on supports of borosilicate glass (including glass coated with Pt, Mo, or a mixture of In and Sn oxides), aluminium, single crystals of silicon, and aluminium oxide. Radiation with λ = 10.6 μm and I = 0.1–1.0 kW cm^{-2} was used. The temperature of the support was 200–650 °C. In studies by Gattuso and co-workers,[64] the main experiments were carried out at T_s = 300 °C, p_{SiH_4} = 800 Pa, W = 70 W, and d = 6 mm. The rate of deposition increased linearly at first, for 60 min, after which a stationary value was established. The stationary value v depends on the rate of consumption of the gas, and with change in the latter from 2 $cm^3 s^{-1}$ to 4 $cm^3 s^{-1}$, v increased from 6.0 nm min^{-1} to 16 nm min^{-1}. The rate of deposition also increased with increase in T_s, W, and p_{SiH_4}. The maximum value of v was limited by the side process of powder formation. The addition of H_2 or HCl to silane was recommended, to suppress homogeneous deposition.

A model of the deposition including the gas-phase decomposition of SiH_4 to SiH_2 and H_2, the diffusion of SiH_2 free radicals to the support, and their reaction on the solid surface to give a deposit has been proposed.[68] In the opinion of the authors cited, the limiting stage is the first of these stages, which determines the exponential dependence of the rate of growth of the deposit on the temperature of the gas T_g. T_g was calculated by assuming that the absorbed energy of the laser beam is equal to the energy lost as a result of thermal conductivity. For pure silane at a pressure p_{SiH_4} = 665 to 1064 Pa, T_s = 200–400 °C, and W = 20–40 W, the value of T_g was 440–550 °C. The dependence of v on T_g gave E_a = 190 kJ mol^{-1}.[69,70] This value coincides with the activation energy of the pyrolysis of SiH_4, and is close to the value 220 kJ mol^{-1} obtained for the decomposition of SiH_4 to Si_2H_6, H_2, and *a*-Si:H powder under the influence of laser radiation with λ = 9.77 μm.[73]

Radiation with λ = 193 nm has been used to obtain an *a*-Si:H coating from disilane.[67,78] At a temperature of the glass support of 200–400 °C and a pressure in the system of 133 Pa, the rate of deposition reached 5.5 nm s^{-1}. The concentration of hydrogen in the deposit depended on T_s, and had the values 17, 9.3, and 7.2 at.% at 200, 300, and 400 °C respectively.

The deposition of germanium from GeH_2 has been carried out[60,62,83] in an assembly with the perpendicular configuration using excimer ArF, KrF, and XeCl lasers (ν = 20 Hz). The laser beam was focussed at a point 1–4 cm from the base of the reactor. By moving the latter along the optical axis, the value of I was varied in the range 1–20 mW cm^{-2}. The duration of the process was about 400 s. Fig. 3 gives the dependence of the initial rate of growth v_0 of the germanium film on the intensity and wavelength of the radiation. The XeCl laser did not induce the reaction. The difference in the action of the radiation of the ArF and KrF lasers is due to the characteristics of the absorption of the radiation by the gas and the deposit. In the opinion of the authors cited,[62] the decrease in v_0 on intensive irradiation is due to the volatilisation of the substance. The average temperature of the support, however, did not exceed 120 °C. It is suggested that a chain reaction is initiated by the two-photon dissociation of GeH_4 to GeH_2 and then takes place according to the scheme shown in Fig. 4. The deposition takes place as a result of the gas-phase diffusion of atomic Ge and Ge_2H_6 to the surface of the support; the concentration of germanium in the gas phase as the support was approached passed through a maximum at a distance of approximately 1.5 mm from it. In the opinion of the authors cited,[83] the low activation energy of this process (E_a = 8.3 kJ mol^{-1}) compared with the pyrolysis of group IV hydrides indicates that the deposition is limited by one of the gas-phase reactions or by the desorption of hydrogen.

An amorphous hydrogenated *a*-SiGe:H alloy was obtained on a support heated to 200 °C by irradiating a mixture of Si_2H_6, GeH_4, and H_2 (λ = 193 nm, τ = 10 ns, ν = 100 Hz, pulse energy E = 15–20 J).[84] Chain radical reactions in the gas phase at a total pressure of 133–250 Pa began as a result of the absorption of one photon by the Si_2H_6 molecule. The intermediate reaction products were Si_2H_5, SiH_3, SiH_2, SiH, and H. The reaction of these radicals with GeH_4 gave $SiGeH_6$, GeH_2, and GeH_3. The proportion of silicon transferred to the deposit was higher than that of germanium.

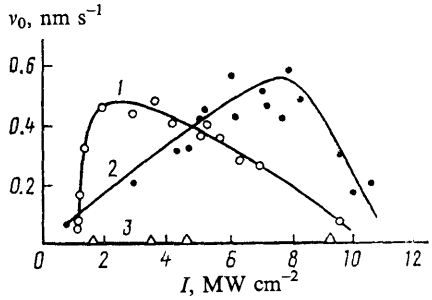


Figure 3. Dependence of the initial rate of deposition of Ge on the energy density of ArF (*1*), KrF (*2*), and XeCl (*3*) lasers.[62]

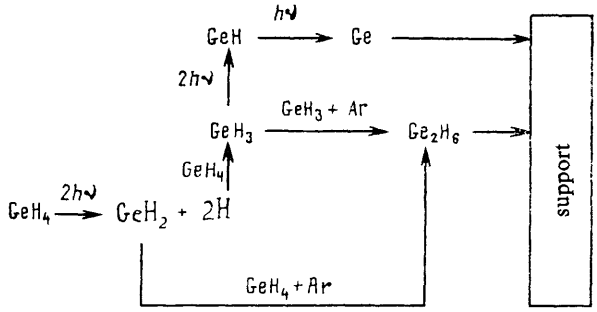


Figure 4. Principal reactions taking place on the irradiation of GeH_4 using a KrF laser (λ = 248 nm).[83]

The rate of decomposition of PH_3 in the optical breakdown of the gas with the formation of a PH_x deposit[85] remains unchanged on going successively from the $P(10)$ line to the $P(32)$ line of a CO_2 laser, and shows a clearly defined threshold. The deposition threshold is determined by the energy and frequency of the pulses, and also by the pressure of PH_3 and the inert gas (Ne).

Data have also been published[86] on the deposition of As from AsH_3, Se from $SeMe_2$, and Te from $TeMe_2$, Te_2Me_2, and $TeEt_2$.

Thus hydrides are most frequently used for the deposition of non-metals. In photolytic processes, radiation in the infrared or visible ranges is used. The principal characteristics of these processes are the increased extent of the kinetic range of the reaction on coordinates concentration–temperature and the possible use of high reagent concentrations without the risk of powder deposition. Photolytic processes are generally carried out in one of three ways: 1) using multi-photon absorption of the radiation of a CO_2 laser (often accompanied by relaxation and heating of the hydride); 2) by chain reactions induced by the absorption of photons with an energy greater than 4 eV; and 3) by optical breakdown of the gas. The last method is apparently complicated by the fact that the threshold conditions of breakdown and the stability of the laser plasma depend to a marked extent on the local composition of the gas and the hydrodynamic characteristics of the system.

III. Deposition of metals

In modern industry, the deposition of metals from the gas phase by the reduction of halides using hydrogen has acquired the greatest importance. In laser-induced chemical deposition, decomposition reactions have found preferential application.

Copper has been deposited from its bis(hexafluoroacetylacetonate) at pressures of 1.3 Pa [87] or 0.4 Pa [88] on silica supports heated by the radiation of an Ar^+ laser. The volume rate of deposition increased from 50 $\mu m^3 s^{-1}$ to 300 $\mu m^3 s^{-1}$ with increase in I from 400 kW cm^{-2} to 600 kW cm^{-2}. The main impurity was oxygen (up to 10 mass %). Au was deposited similarly from its dimethyl(pentane-2,4-dionate) at a pressure of 1.0 Pa; at I = 400 kW cm^{-2} the rate of the process was 1 $\mu m\ s^{-1}$.[89]

Zinc and cadmium have been deposited using $ZnMe_2$ and $CdMe_2$. The thermal and spectral properties of these compounds are similar,[90,91] so that they show identical behaviour in laser decomposition processes. These processes can be examined for the case of the deposition of cadmium.[48,92–104]

The radiation of a Kr^+ laser with λ = 520.8–568.2 nm has been used to heat GaAs supports.[98] At W = 70–300 mW and d = 10 μm the temperature of the support was 235–1000 °C. The process was carried out by decomposing $CdMe_2$ at atmospheric pressure in a hydrogen carrier; the partial pressure of $CdMe_2$ was 20 Pa. The cadmium deposit obtained at T_s < 550 °C was formed within the focal spot. At higher values of T_s, the deposition also took place beyond its limits. A typical rate of deposition was 20 nm s^{-1}.

When radiation with a shorter wavelength, λ = 257 nm, was used, the process took place mainly by the non-thermal decomposition of $CdMe_2$, and mainly in the gas phase, and not in the adsorbed layer. The rate of deposition was linearly dependent on the partial pressure of $CdMe_2$ and the intensity of the irradiation. At I > 2 W cm^{-2}, a deviation from the linear relationship towards lower values of v was observed, due to the decreased concentration of the reagent in the volume of the laser beam. The addition of an inert gas led to a sharp decrease in the total rate of deposition as a result of the decreased rate of gas-phase diffusion of atomic cadmium to the surface of the support. Under these conditions, the role of adsorbed $CdMe_2$ increased, with a simultaneous increase in the sensitivity of the process towards energetic non-uniformity of the surface and interference of the incident and reflected laser beams.[97]

When radiation with λ = 193 nm was used, the deposition took place only as a result of the decomposition of $CdMe_2$ in the gas phase.[99] The concentration of Cd in the gas phase on irradiation with a pulse ArF laser was proportional to I, corresponding to single-stage photodissociation. A definite role was also played, however, by processes in the adsorbed layer, which the authors cited[99] called "prenucleation". In an experiment in which the support (Si or SiO_2) was kept in a $CdMe_2$ atmosphere, the

non-adsorbed $CdMe_2$ was removed, and the support was irradiated by a beam with a characteristic shape, the formation of a deposit was not observed. The reaction vessel was then filled with $CdMe_2$ again to a pressure of up to 0.20 kPa, and the support was irradiated by a broad uniform beam. This gave a deposit whose shape coincided with that of the beam used in the first stage of the experiment. If however in the first stage the irradiated support did not carry an adsorbed layer of $CdMe_2$, a deposit with the characteristic shape was not formed in the second stage.

Aluminium has been obtained by decomposing the compound $AlC_{12}H_{27}$,[105,106] but more frequently by decomposing $AlMe_3$.[10,11,14,98–100,105–110] As with $CdMe_2$, several types of radiation have been used for the deposition.

For example, when a GaAs support was heated to 400 °C by the radiation of a continuous Kr^+ laser with λ = 520.8–568.2 nm, and a mixture of hydrogen and $AlMe_3$ with a partial pressure of 1.3 kPa was passed through the reaction vessel at atmospheric pressure, rods with a diameter of 20–90 μm were obtained at the focal spot.[98] The deposit contained amorphous Al and crystalline Al_3C_4. The length of the rods depended on the intensity of the radiation, and did not exceed 0.5 mm. The roughness of the surface of the rods obtained was attributed[98] to the turbulence of the gas stream. Change in the gas consumption from 1.0 litre h^{-1} to 4.4 litre h^{-1}, however, had no influence on the course of the process or the form of the deposit. The rate of growth of the rods decreased continuously with time (for example, in the first 120 s the rate decreased from 7 μm s^{-1} to 1 μm s^{-1}) as a consequence of the non-isothermal nature of the process; with increase in the thickness of the layer, the growth surface moved out of the focus, and the intensity of irradiation (and hence the temperature) decreased. When the beam was focussed at a point 30 μm from the surface of the support, an increase in the rate of growth to a maximum value at the focus of the laser beam was observed at first, after which the rate decreased.

In the range 442–460 nm, $AlMe_3$ has three absorption bands at 443.6, 445.1, and 446.2 nm. Radiation with these wavelengths has been used to deposit aluminium.[100] A potential of up to 2 kV was applied to the support to attract the ions. The latter reached the surface having a higher energy, and this increased considerably the quality of the coatings obtained.

Radiation with λ = 257 nm did not lead to heating of a support of silicon or its oxide, but acted directed on $AlMe_3$ in the gas phase or in the adsorbed layer.[10] At room temperature and a pressure of several hPa, trimethylaluminium is extensively dimerised. The quantum yield of aluminium in the gas phase was appreciably lower than that in the adsorbed layer.

At λ = 248 nm, Al atoms in the gas phase are formed by a cascade process, each stage of which is initiated by one-photon absorption.[109] The main chain of transformations is described by the scheme

$$Al_2Me_6 \rightarrow AlMe_3 \rightarrow AlMe_2 \rightarrow AlMe \rightarrow Al.$$

C_2H_6 is a side product of the deposition.

An advantage of the use of radiation with λ = 193 nm is that when it is directed on to the surface, a high quantum yield is achieved in the non-thermal photo-desorption of methyl groups. This makes it possible to obtain highly pure aluminium.[107]

The reactions of $GaMe_3$ and $InMe_3$ in the visible and ultraviolet ranges are similar.[111–113] The deposition of In by the decomposition of InI at λ = 193 nm has also been proposed.[114] The deposit, with a thickness of 0.3 μm, did not contain iodine.

Tetraethyllead has an absorption band at 242 nm, and is characterised by an appreciable photon absorption cross-section at 257.3 nm. The rate of deposition of lead at this wavelength is directly proportional to the $PbEt_4$ pressure and the intensity of the radiation; at p_{PbEt_4} = 500 Pa and I = 600 W cm^{-2}, the rate of deposition reaches 8 nm s^{-1}.[115] Increase in the partial pressure of He from 13.3 kPa to 79.8 kPa leads to an almost two-fold decrease in the rate of deposition. This is due to the decrease in the rate of diffusion of Pb atoms in the gas phase, which indicates that a predominant role is played by photolytic decomposition.[115]

Titanium has been obtained by decomposing its tetrachloride on supports of $LiNbO_3$ and SiO_2 at the focal spot (d = 4 μm) of a quasi-continuous Ar^+ laser (W = 5 mW, λ = 257 nm).[32] At an intensity of radiation of 50 kW cm^{-2}, the temperature in the spot did not exceed 30 °C. In the opinion of the authors cited,[32] the main reactions take place in the adsorbed layer. Irradiation of gas with a high concentration of the tetrachloride ($\geqslant$1.0 kPa) or gas containing hydrogen leads to the reduction of $TiCl_4$ to $TiCl_3$ and its deposition on the surface of the support as "hail". Sharp focussing of the radiation on the surface suppresses the gas-phase deposition, and the reactions in the adsorbed layer are complete with the formation of metallic titanium. In this case the deposition mechanism is possibly autocatalytic.[32]

Chromium can be obtained by decomposing its hexacarbonyl.[14,116–119] The use of radiation with λ = 248 nm gave black fragmentary films with a columnar structure in an assembly with the parallel configuration, and light silvery coatings in an assembly with the perpendicular configuration.[14] The main impurity was oxygen (up to 7 mass %), but its concentration can be decreased by using an improved reactor and an improved vacuum system.

The decomposition of $Cr(CO)_6$ under the influence of radiation with wavelengths of 193, 249, and 308 nm has been carried out with both the parallel and the perpendicular relative arrangements of the beam and the support.[118] In the last case, coatings with strong adhesive power were obtained on quartz, Pyrex, Suprasil, and aluminium. At τ = 10 ns, E = 8–12 mJ, and ν = 10–60 Hz, the pulse rate of deposition was independent of ν, and had the values 0.010, 0.028, and 0.005 nm $pulse^{-1}$ for λ = 193, 249, and 308 respectively (the thickness of the coatings did not exceed 300 nm).

Japanese workers[119] obtained chromium films on an assembly with the perpendicular configuration (λ = 248 nm, ν = 50 Hz, I = 1–9 MW cm^{-2}, average energy density 140 J cm^{-2}). The quartz support was not heated specially during the process. The deposition was carried out from argon at atmospheric pressure and $p_{Cr(CO)_6}$ = 40–90 Pa. The deposits contained approximately 50% chromium, 20–50% oxygen, and up to 30% carbon, depending on the intensity of the radiation. The films with the lowest concentration of oxygen had a metallic lustre and strong adhesive power, but their electrical conductivity was lower than that of chromium by a factor of 500. The purity of the films obtained was much lower than that of the coatings described by Boyer and co-workers,[14] apparently due to the high partial pressure of Ar in the reactor.

Molybdenum has been obtained from $Mo(CO)_6$.[14,116,118,120,121] At a low temperature of the support, the deposit contained large quantities of oxygen and carbon. Thus the pulse irradiation (λ = 248 nm) of molybdenum carbonyl adsorbed on Si (100) gave at 150–200 K a deposit with the composition $MoCO_{0.3}$ with a quantum yield close to 1.[120] By comparing the deposition processes taking place at room temperature under the influence of radiation with λ = 157, 193, 248, and 308 nm, Solanki and co-workers[116] found that the lowest concentration of carbon in the deposit and the

highest rate of deposition were achieved at 248 nm. According to Flynn and co-workers,[118] however, the rate of deposition at 193 nm is slightly greater than that at 248 nm.

The deposition of Mo by the optical breakdown of the gas using the radiation of a pulse CO_2 laser has been described.[121] Argon was added to the gas to facilitate breakdown.

Tungsten deposits have been obtained by two reactions: by decomposing tungsten carbonyl,[14,116,118,122] and by reducing tungsten hexafluoride with hydrogen.[122–127]

The deposition of tungsten from its carbonyl is similar to that of molybdenum. The rate of deposition at 257 nm increases in proportion to the increase in I to 1 kW cm^{-2} (Fig. 5). At λ = 193 nm, other conditions being equal, the rate of deposition is three times greater.[118]

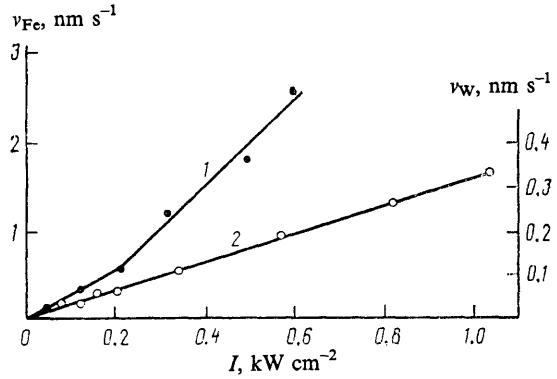


Figure 5. Dependence of the rate of deposition of W (*2*) and Fe (*1*) on a quartz support on the intensity of radiation with λ = 257 nm at pressures $p_{W(CO)_6}$ = 27 Pa and $p_{Fe(CO)_5}$ = 67 Pa.[128]

Tungsten has been deposited from WF_6 by irradiating a quartz support with a CO_2 laser with a power of 40 W.[122] Under these conditions, the greatest thickness of the tungsten film obtained was limited to 250–500 nm, depending on the conditions of irradiation and the concentration of the reagents. Three stages of the process are readily distinguished: 1) induction, 2) intensive, 3) attenuated. The duration of the induction stage decreases with increase in the radiation power; this can be attributed to the increased rate of attainment of the "threshold temperature" of the surface of the support. The second stage is short; it corresponds to the attainment of the maximum rate of deposition, the magnitude of which depends on I (or more accurately on T_s) and p. The decrease in the rate of deposition in the third stage is due to the decrease in the temperature of the support as a result of the reflection of the radiation by the tungsten film formed. Increase in the intensity of the radiation should of course have led to continuation of the deposition process, but this possibility was not studied experimentally.

The deposition of tungsten on a silicon support heated by the radiation of a Kr^+ laser (λ = 468–530 nm), not absorbed by the gaseous reagents (p_{H_2} = 53.2 kPa, p_{WF_6} = 26.6 kPa), has been described.[123] The beam with a power of 3–4 W was focussed on the support to give a spot with a diameter of 20 μm, and moved over the surface at a rate of 0.2–2.0 mm s^{-1}. With slower movement and a power greater than 4 W, fusion of silicon was observed. Since in the wavelength range used Si and W have similar absorbing power, it was possible to obtain thick deposits and to grow coatings by repeated irradiation. Similar results were obtained by other workers.[126]

Manganese has been obtained by decomposing $Mn_2(CO)_{10}$ under the influence of radiation with a power of 1–40 mW (λ = 337.4–356.4 nm, I = 3–150 kW cm^{-2}). When the beam scanned a ZnS support heated to 100 °C, bands of Mn with a thickness of 30–800 nm were deposited.[129]

$Fe(CO)_5$ has been used to obtain iron coatings.[122–124,127] The irradiation of a quartz support with a CO_2 laser with a power of 5.5 W gave the same self-limiting process as in the deposition of tungsten from its hexafluoride. Thus at $p_{Fe(CO)_5}$ = 3.6 kPa, the thickness of the film after 3 ms was 50 nm, which did not increase on subsequent irradiation. An interesting feature is that for a lower radiation power, the growth was more prolonged; for example, for a radiation power of 2.2 W, a coating with a thickness of 1 μm was formed in 1 s. The radiation of an Ar^+ laser has also been used to heat the support.[130]

In the ultraviolet range, photolytic deposition of iron takes place. The use of radiation with λ = 257 nm led to the continuous growth of the deposit at a rate which depended on the intensity of the radiation (see Fig. 5). The break on the straight line apparently indicates a change in the deposition mechanism.[128] The decomposition of $Fe(CO)_5$ has also been carried out using the fourth harmonic of a neodymium laser (λ = 266 nm, τ = 15 ns, ν = 25 Hz, W = 0.01–0.3 mW).[131] The film, deposited in a focal spot with d = 150 μm, had strong adhesive power, but the film deposited beyond the spot had low adhesive power. This indicates that the deposition was not due to the thermal decomposition of the carbonyl. The rate of deposition at p = 130 Pa and W = 0.25 mW was 0.25 nm s^{-1}; it decreased non-linearly with increase in the Ar pressure to 80 kPa, and increased in proportion to p and W. In the opinion of the authors cited, this indicates an unsaturated one-photon decomposition mechanism.

Nickel has been deposited from $Ni(CO)_4$.[8,123,124,132–136] When a quartz support was irradiated by a low-power CO_2 laser, self-limitation of the deposition was observed.[123,124,132,136] The maximum rate of deposition increased non-linearly with increase in the power from 0.3 μm s^{-1} at W = 0.4 W to 3 μm s^{-1} at W = 2 W. The dependence of the duration of the induction stage on the intensity of the radiation indicates that the reaction rate is determined not only by the temperature of the support. For a high value of I, a decisive influence on the course of the deposition may be shown by the rates of nucleation and the gas-phase reactions.[124] The activation energy of the deposition of nickel on steel, glass, and silicon supports was 90 kJ mol^{-1}, which is characteristic of a pyrolytic process. When the radiation of a Kr^+ laser was used, the diameter of the undulating deposit was much greater than the value of d, and increased during continuous radiation, evidently as a result of the heating of the non-irradiated parts of the support due to its thermal conductivity. The dependence of the rate of growth of the Ni rods on I is shown in Fig. 6. It can be seen from Fig. 6 that deposition does not take place below a certain threshold value of I. This is followed by a plateau, on which the rate of deposition remains unchanged, after which it begins to increase with subsequent increase in I. When helium, which has a high thermal conductivity, is added to the reactor, the rate of deposition decreases as a result of

the cooling of the surface by the increase in the removal of heat.[133,135] The nickel specimen obtained in this way does not contain carbon (accuracy of the determination 1%). Its electrical resistance is 1.9×10^{-5} Ω.cm (three times the tabulated value), indicating that the deposit is highly pure.

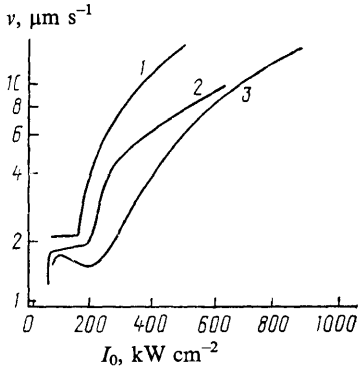


Figure 6. Dependence of the rate of growth of Ni rods on the intensity of the radiation at $p_{Ni(CO)_4}$ = 40 kPa and different focus spot diameters, μm: *1*, 22, *2*, 27, *3*, 13.5; in the experiments corresponding to curve *2*, He was added to $Ni(CO)_4$ (p_{He} = 53.3 kPa).[133]

Platinum has been deposited from $Pt(PF_3)_4$ at a pressure of 60 Pa on silicon, aluminium, graphite, quartz, and copper supports using a pulse Kr^+ laser.[137,138] The yield of the deposit decreased in the order of the supports given above (energy density in each pulse 200 mJ cm^{-2}). The quantum yield of platinum amounted to thousandths of the original quantity of $Pt(PF_3)_4$ (for example, 3.7×10^{-3} on the aluminium support). It was shown that the deposition takes place under the influence of electrons produced by the interaction of the laser radiation with the surface of the support.[137,138] The similar decomposition of $Fe(CO)_5$ and $CoEt_2(CO)_2$ under the influence of slow photoelectrons on the irradiation of glass and silver supports with the light of an Xe–Hg lamp (λ = 200–400 nm) has been described.[139] The other reactions examined above possibly also take place by this photoelectron mechanism.

Thus the metals of groups I, II, and III are most frequently deposited from organometallic compounds, and metals of groups VI, VII, and VIII from their π-complexes. The efficiency of the photolytic decomposition of these compounds at different values of λ correlates with the form of the absorption spectra. The deposits generally contain appreciable quantities of carbon and oxygen, which apparently originate in the ligands and in the air entering the reaction vessels. Dilution of the reagents with large quantities of inert gases leads to a significant decrease in the total rate of deposition and in the purity of the deposits. In contrast to the deposition of non-metals, an additional photoelectron mechanism operates in the deposition of metals.

IV. Deposition of inorganic compounds

Silicon carbide has been deposited using a CO_2 laser and a mixture of H_2 and $SiMeCl_3$.[9,50] Radiation with a power of 25 W was focussed on the surface of W, SiC, C, SiO_2, and ZrO_2 supports, so that the temperature reached 1100–1450 °C. The rate of deposition was directly proportional to p_{SiMeCl_3} in the range 0.27–13.3 kPa and inversely proportional to p_{H_2} in the range 0–10.6 kPa. The material of the support had no influence on the rate of deposition at a deposit thickness greater than 1.0 nm. The value of E_a in the absence of H_2 was 335 kJ mol^{-1}, and at p_{H_2} = 13.3 kPa, E_a was 400 kJ mol^{-1}. In the opinion of the authors cited,[9,50] the limiting stage was the decomposition of the methyl radical. The deposit was polycrystalline, and the particle size depended on the temperature of the process. Silicon carbide has also been obtained by decomposing $SiMeCl_3$ and $SiMe_2Cl_2$ on crystalline glass supports heated by the beam of an Ar^+ laser.[140] The rate of growth of the rods reached 70 μm s^{-1}. Stoichiometric SiC was deposited from $SiMe_2Cl_2$ in a nitrogen atmosphere. In a CO_2 atmosphere, codeposition of silicon and its dioxide took place. The decomposition of $SiMeCl_3$ in a stream of nitrogen led to the formation of graphite.

SiC powder has been synthesised from a mixture of SiH_4 and C_2H_4, which absorb radiation with λ = 10.59 μm.[141] In the tubular reaction vessel, the beam of a CO_2 laser with a diameter of 6 mm was directed at right angles to the stream of reagents. At the point of intersection, I = 530 W cm^{-2}, and T_g = 1100 °C. In a narrow beam (d = 2 mm) the corresponding values were 5.25 kW cm^{-2} and 1550–1750 °C. Since the time for which the reagents were in the reaction zone was constant, the diameter of the particles of the powders obtained showed little scatter. The chemical composition of the deposit could be varied by altering the reagent ratio, pressure, and intensity of the radiation.[141]

The formation of surface periodic structures from a mixture of SiH_4 and CH_4 at the points of a surface interference wave at λ = 9.27 μm has been described.[142]

The deposition of titanium carbide[127,132,143] using a carbon steel support required the powerful radiation of a CO_2 laser (0.5–1.2 kW in a spot with d = 1–2 mm). The original mixture consisted of $TiCl_4$ (1.6 kPa), CH_4 or C_2H_2 (26.6 kPa), and, sometimes, H_2 (26.6 kPa). The presence of H_2 was not necessary for the deposition of the carbide.

Titanium silicide was obtained similarly using SiH_4 instead of the hydrocarbon.[144–147] The single-crystal silicon support was heated to 400–500 °C by the radiation of a CO_2 laser with a power of 160 W. In addition, the gas was irradiated by an ArF laser (I = 100 MW cm^{-2}). Increase in the molar ratio SiH_4:$TiCl_4$ from 3 to 18 led to a change in the Si:Ti ratio in the deposit; for example, at T_s = 400 °C this ratio changed from 1.0 to 2.3. The silicide was amorphous at 400 °C, and partly crystalline at 450 °C and 500 °C. The concentration of oxygen in the deposit was 2–4 at.%, and the chlorine concentration 0.2 at.%.

Zinc oxide has been deposited in an assembly with the parallel configuration from a mixture of dimethylzinc and oxides of nitrogen, using radiation with λ = 248 nm with N_2O, and radiation with λ = 193 nm with NO_2.[14,148] The highest purity of ZnO and the highest rate of its deposition were achieved at a total pressure of 266 Pa and a $ZnMe_2$ partial pressure of 4.0 Pa. The temperature of the support varied from 20 °C to 220 °C. The coatings, with a thickness of 0.5 μm, contained less than 1% carbon and traces of nitrogen. Increase in the ratio $ZnMe_2$:NO_2 led to a change in the stoichiometry of the deposit, and this was reflected in its electrical conductivity

(the extreme values of the electrical conductivity differed by a factor of 10^4).

Aluminium oxide was deposited similarly. 50–1000 $cm^3 s^{-1}$ N_2O, 100 cm^3 s^{-1} He, and $AlMe_3$ at a partial pressure of 10.6 Pa were passed through the reaction vessel at a pressure of 133 Pa.[149] A blue fluorescence was observed along the laser beam. The rate of deposition was approximately 200 nm min^{-1} at W = 10 W and λ = 248 nm. At W = 8.2 W and λ = 193 nm, the rate was higher, but the deposit was less uniform along its thickness. The coatings obtained at a rate of deposition of 1 μm min^{-1} separated from the support on contact with air. Loose grey films were obtained at a high rate of deposition. The best coatings, containing less than 1% carbon, were obtained at T_s = 450 °C, p_{AlMe_3} = 10–15 Pa, and an N_2O consumption of 200–800 cm^3 s^{-1}.

Al_2O_3 was deposited from a mixture of $AlMe_3$ and NH_3 at a support temperature below 100 °C (radiation with λ = 193 nm was used).[150] The source of oxygen was the air entering the reactor. At a support temperature above 100 °C, ammonia became chemically active, and up to 400 °C the deposit formed consisted of a mixture of Al_2O_3 and AlN.

The preparation of indium and gallium oxides by methods similar to that used for Al_2O_3 has been proposed.[149]

Silicon oxide has been deposited in an assembly with the parallel configuration by irradiating a mixture of SiH_4 and N_2O using an ArF laser (λ = 193 nm).[14,151] At a pulse frequency of 100 Hz, the average intensity of the radiation was 40 W cm^{-2}. The laser beam passed over the support at a distance of 0.3 mm. The pressure in the reactor did not exceed 1.0 kPa. The consumption of N_2O was 800 cm^3 s^{-1}, and the consumption of N_2 containing 5% SiH_4 was 70 cm^3 s^{-1}. The silicon support was heated from 20 °C to 600 °C. The deposits obtained at temperatures up to 200 °C appeared non-uniform, and readily separated from the support. At $T_s \geqslant$ 250 °C, uniform strong deposits were obtained. The rate of deposition reached 5 nm s^{-1}. The concentration of nitrogen (as Si_3N_4) was less than 5 mass %, and the concentration of hydrogen (combined with Si atoms) was 1–4 at.%.

SiO_2 coatings were obtained similarly.[152] The laser beam has a cross-section of 5 × 20 mm, and the pulse frequency was varied from 3 Hz to 70 Hz. The dependence of the rate of deposition v on the partial pressure of N_2O was non-linear, and had a maximum at p_{N_2O} = 3.0 kPa. The rate was directly proportional to the power of the pulses. The rate of deposition was also influenced by the $N_2O:SiH_4$ ratio. With increase in the latter, the rate increased, but only to a limiting value. This saturation phenomenon is due to the existence of a limit to the transport properties of SiH_4. According to some authors,[152] the highest rate of deposition was observed at $N_2O:SiH_4$ = 50, and according to others,[153] at $N_2O:SiH_4$ = 20 (deposition in the absence of N_2 diluent). Analysis of these values led the authors cited[152] to the conclusion that the quantum yield of the photodissociation of N_2O is close to 0.01, but that the O atoms liberated in turn initiate the additional dissociation of N_2O or react with N_2O to form more photosensitive compounds, for example NO or NO_2. As a result, the extent of the transformation of N_2O to yield O is increased two-fold.

Titanium oxide has been obtained by the reaction of $TiCl_4$ with CO_2 in hydrogen by heating a quartz support by the radiation of a carbon dioxide laser with a power of 5–10 W.[6,8,127,132,144] The partial pressure of the reagents was $TiCl_4$ 1.65, CO_2 2.73, and H_2 2.73 kPa. The rate of deposition had values of 30–100 nm s^{-1} (d = 0.8–3.0 mm, τ = 0.1–1.0 s). Titanium dioxide absorbs radiation more strongly than SiO_2, so that repeated pulse irradiation of the same section of the surface gave a thicker deposit than continuous irradiation with the same duration. Moreover, on continuous irradiation the form of the surface of the deposit resembled a Gaussian curve, whereas on pulse irradiation (for example with 20 pulses in 0.1 s), the deposit had the form of a plateau; this can apparently be attributed to the ratio of the rates of diffusion and heat transfer.

Titanium oxide can be obtained by decomposing oxygen-containing organometallic compounds, for example $Ti(OCHMe_2)_4$.[154]

The laser-induced decomposition of CrO_2Cl_2 has been studied.[155] Radiation with λ = 488–515 nm was focussed on a spot with a diameter of 5 mm or 2 mm on supports of glass, fused SiO_2, or single crystals of Si and Al_2O_3. The radiation power varied from 1 mV to several W, and the CrO_2Cl_2 pressure was 13 Pa. Mass spectrometry detected an appreciable quantity of chlorine atoms in the irradiated gas. This indicates an appreciable rate of photolytic decomposition of the oxide chloride, although CrO_2Cl_2 itself absorbs at λ = 420 nm. To study the heterogeneous reactions, an irradiated fused SiO_2 support was placed in the chamber of the mass spectrometer, and the measurements were made during the reaction. The deposition took place in three stages. In the first stage, which lasted tens of seconds, slow growth of the CrO_2 film took place, and this process was accompanied by the production of a small flux of chlorine atoms. The deposition apparently involved the decomposition of CrO_2Cl_2 molecules in the gas phase or in an adsorbed layer. In the second stage, the flux of the species Cl, Cl_2, and O_2 increased sharply. The increase in the rate of the process was due to the thermal activation of the decomposition of CrO_2Cl_2 as a result of local heating of the surface by the absorption of radiation by the deposit formed in the first stage. The spontaneous acceleration took place until the thickness of the deposit was greater than the characteristic thickness of the absorbing layer. This was followed by the third stage, characterised by a stationary rate of deposition with a new increased surface temperature. Since the deposit contained Cr_2O_3, and O was detected in the gas phase, in the second and third stages the deposition was accompanied by the thermal decomposition of CrO_2, which takes place at temperatures above 400 °C. At a radiation intensity lower than 1 W cm^{-2}, only the dioxide was deposited.

Experiments carried out with the radiation of an excimer laser (λ = 193 nm) at a CrO_2Cl_2 pressure of 13 Pa showed that the composition of the deposit can be regulated by adding HCl to the gas phase; the deposit had the composition $CrO_{0.83}$ at an HCl pressure of 26.6 kPa, and $CrO_{1.5}$ in the absence of hydrogen chloride.[155]

Films of WO_3 or Fe_3O_4 have been deposited by irradiating (λ = 308 nm) a mixture of NO_2 with $W(CO)_6$ or $Fe(CO)_5$ in a reactor heated to 50 °C.[156] The carbonyls were mixed with an inert gas (Ne or He), whose partial pressure was 70–90 kPa. The deposition of WO_3 was more rapid than that of Fe_3O_4, since the absorption cross-section of $W(CO)_6$ is almost 10^2 times that of $Fe(CO)_5$.

Aluminium nitride has been deposited in an assembly with the parallel configuration from a mixture of $AlMe_3$ and NH_3 (λ = 193 nm).[150] Ammonia reacted at a support temperature above 100 °C, and with increase in the support temperature to 400 °C the mole fraction of AlN in the deposit increased almost linearly, reaching 1. Practically pure nitride was deposited at 400–500 °C.

Amorphous films of silicon nitride were obtained in assemblies with the parallel configuration from a mixture of SiH_4 and NH_3.[157] The radiation of a CO_2 laser with a power of up to 160 W (λ = 10.6 μm) was used. The temperature of the Si support was

250–450 °C, and the pressure in the reactor 1.33–2.0 kPa. The Si:N ratio in the deposit depended on the reagent ratio, and was 1.2 at $SiH_4:NH_3$ = 1000. The infrared spectrum of the deposit contained bands characteristic of Si–N, Si–H, Si–O, and N–H bonds. The concentration of hydrogen in the deposit decreased with increase in the temperature of the support. The rate of deposition was low (15 nm min^{-1}), and independent of temperature.

Coatings were obtained[158] using a low-power ArF laser (W = 0.2 W). The rate of deposition of the coatings on an area of 7.5 cm^2 was independent of the temperature of the support (200 to 600 °C), and equal to 5 nm min^{-1}. A similar study[14] showed that the rate of deposition may reach 70 nm min^{-1} (temperature of the support 200–425 °C, pressure in the reactor 266 Pa, gas consumption (cm^3 s^{-1}): SiH_4 10, NH_3 10, N_2 50). The Si:N ratio in the deposit was less than 1, the hydrogen concentration 20–30 at.%, and the oxygen concentration did not exceed 5 at.%.

The deposition of indium phosphide from the trimethyl compounds (on supports of Si, InP, InGaAs, and GaAs) was carried out using an excimer laser (E = 100–200 mJ, τ = 15 ns, ν = 20 Hz).[159–161] The dependence of the nature of the deposition on the wavelength was studied at T_s = 323 °C, a total pressure of 0.8 kPa, and gas consumptions of (cm^3 s^{-1}): Me_3InPMe_3 9, PMe_3 38, H_2 150, and He 230. At 351 nm, the reagents were transparent, but a small quantity of deposit consisting of In and O was obtained. Radiation at λ = 248 nm was absorbed by $InMe_3$, so that mainly indium was deposited. At 193 nm, both reagents absorbed radiation strongly, and InP was deposited. A typical rate of deposition was 0.03 nm $pulse^{-1}$. The composition of the deposit depended on the photon flux: a phosphorus deficit was observed at 0.01–0.03 J cm^{-2}, and a deposit with the stoichiometric composition (InP) was formed at 0.1–0.3 J cm^{-2}. The deposit obtained for a low value of the flux was amorphous, but at values greater than 0.1 J cm^{-2} it was polycrystalline, with a particle size of 5–40 nm.

Gallium arsenide has been deposited by the reaction[143]

$$GaMe_3 + AsMe_3 + H_2 \rightarrow GaAs + 2CH_4.$$

The partial pressures of $GaMe_3$, AsMe3, and H_2 were 8.6, 13, and 20 kPa respectively. The SiO_2 support was heated at the focal spot (d = 0.6 mm) to 600–900 °C by the radiation of a CO_2 laser with a power of 2–3 W for 2–12 s. At W = 3 W, the deposition took place in a ring round the centre of the beam, and the deposit was not continuous even when the thickness reached several μm. The rate of deposition was 15–50 nm s^{-1}. The composition of the deposit varied form $GaAs_{0.37}$ to $GaAs_{2.4}$, depending on the irradiation conditions.

The deposition of GaAs was carried out at atmospheric pressure from a mixture of AsH_3 and $GaMe_3$ (or $GaEt_3$) by heating supports of single-crystal Si or GaAs to 500 °C with the beam of an Ar^+ laser (I = 1.5–35 kW cm^{-2}).[162,163] Scanning with the beam gave bands with a width of 1.5–500 μm and a thickness from 20 nm to 4 μm. Auto-epitaxy was observed at a growth rate lower than 2 nm s^{-1} (high rate of scanning and low exposure in one scanning cycle).

Stepwise layer growth of GaAs took place with the mixture of $GaMe_3$, AsH_3, and H_2 (total pressure 1 kPa) was supplied intermittently with a cycle duration of 4 s.[164] A section of the support was heated intermittently to 200–500 °C by the radiation of an Ar^+ laser. In this process, the proportion of deposited Ga was 1.0, and the activation energy was the same as that without irradiation (87 kJ mol^{-1}). A model of stepwise layer epitaxy, which assumes that photocatalytic decomposition of $GaMe_3$ takes place only on the surface As atoms (but not Ga atoms) was proposed.

The auto-epitaxy of GaAs in an $AsCl_3–Ga–H_2$ gas mixture was studied using excimer KrCl, KrF, XeCl, or XeF lasers at ν = 5–70 Hz.[165] Only the radiation with λ = 249 nm increased the rate of the process (for example by a factor of almost 4 at T_s = 600 °C and W = 1.7 W); the rate of deposition was proportional to the radiation power, and had values of 0.6–1.4 nm s^{-1}. The increase in rate is apparently due to the photolytic reduction of $AsCl_3$ by hydrogen to AsCl, as confirmed indirectly by the form of the infrared spectra.

Finally, it may be noted that there are three main methods for depositing compounds: 1) the simultaneous deposition of the elements of the compound being deposited (for example, from a mixture of SiH_4 and C_2H_4, or $GeMe_3$ and AsH_3); 2) the codeposition of a substance which is gaseous under the conditions of the experiment (oxygen, nitrogen) with another substance being deposited (for example from mixtures of $ZnMe_2$ and NO_2, or SiH_4 and NH_3); and 3) the decomposition of a complex compound with preservation of the bond between the elements being deposited [for example CrO_2Cl_2 or $Ti(OCHMe_2)_4$]. Formally, the reactions involving $MeSiCl_3$, Me_2SiCl_2, and Me_3InPMe_3 are of the last type, but in fact these compounds undergo preliminary decomposition in the gas phase, so that in reality they are of the first type.

V. Characteristics of laser-induced chemical deposition reactions

The experimental data examined reveal various characteristics of laser-induced chemical deposition from the gas phase.

1. These reactions require radiation with a definite wavelength. To transfer the molecules to higher vibrational levels, the wavelength of the radiation should lie in a relatively narrow range of values (about 0.1 μm). For example, the decomposition of silane by this method requires radiation with λ = 10.59 μm, and even at 10.55 μm the photolytic reaction does not take place. On the other hand, to transfer molecules to an excited electronic state, there is a restriction only on the maximum wavelength (minimum photon energy). The experimental data indicate that in this case it is appropriate to use photons with an energy 1.2–2.0 times the bond energy.

2. The principal parameters of the deposition: the intensity of the radiation, concentration of the reagents, pulse duration, and pulse repeat frequency, show clearly defined threshold values. Below these values, only gas-phase reactions, which probably have their own restrictions, can take place.

3. Deposition takes place most readily on irradiation of the support; prenucleation is observed close to the threshold parameters, that is a small quantity of new substances is apparently formed using the surface energy of the heterogeneous support. Another way of bringing about the process is by the irradiation of the gas close to the support, when the latter acts as a "sink" for the active species generated. Finally, the process takes place with the greatest difficulty in the reaction zone in the absence of any surfaces, since homogeneous nucleation requires a relatively high supersaturation.

4. Redistribution of the absorbed laser energy before the start of the chemical transformations leads to heating of the gas and transfer of the process to a known thermochemical path. Similarly, the absorption of radiation by the deposit formed makes probable a change from a photolytic to a pyrolytic mechanism (an example is

provided by the decomposition of chromium oxide chloride). If neither the support nor the deposit absorb radiation, the rate of the process is not sensitive to the temperature of the support; formally, this means that the apparent activation energy is zero.

5. In the deposition of compounds, their composition depends not only on the ratio of the starting materials but also on their comparative photo-activity; this provides an additional "lever" for controlling the properties of the substance obtained.

6. Under certain conditions, laser radiation leads to the formation of a plasma either as a result of optical breakdown of the gas or as a result of the emission of photoelectrons from the irradiated support, so that the deposition becomes strictly plasmochemical.

These characteristics are listed with traditional chemical deposition from the gas phase in mind.

VI. Possible applications of laser-induced deposition processes

The reactions examined are used mainly to obtain fine powders,[166–175] amorphous, polycrystalline, and single-crystal films (layers, coatings),[19,57,150,165,176–180] narrow bands of unlimited length,[50,123,133,154,181–183] regular surface structures,[184–186] and parts for drawing optical fibres.[187,188] These products have potential uses in powder metallurgy, solar energy, micro-electronics, radio technology, applied optics, and the technology of protective and decorative coatings. In each of these fields, a new technological method generally has to compete with several well established and intensively developing technologies. Thus a number of methods of deposition from liquid, gas, and plasma are used successfully to obtain fine monodisperse powders.[189] In micro-electronics, surface structures are deposited using ultraviolet and X-ray lithography, and continuous films are obtained by chemical reactions with gaseous reagents, including chemical deposition from the gas phase,[190] and also ion implantation.[191] In the preparation of elements based on *a*-Si:H, the main competing method is plasmochemical deposition.[192] Optical coatings are obtained by a range of methods: physical[193] and chemical[194] deposition, including atomisation in a glow discharge, ion-beam and magnetron atomisation,[195] and laser volatilisation.[196]

The lack of the required data makes it impossible to carry out a comparative economic evaluation of different methods. According to one estimate,[169] the cost of the production of 1 kg of silicon, silicon carbide, and silicon nitride powders in an assembly with an output of 50 ton per year using a CO_2 laser with a power of 1.5 kW is 5–25 dollars (the wide range of values is due to the difference in the cost of silane, whose contribution is considerable). The production of these powders might be economically advantageous with lasers operating for many hours (ideally, many days), but this is as yet impossible.

Thus it appears unlikely that there will be any significant practical application of laser-induced chemical deposition in the foreseeable future. The situation is slightly more optimistic for the small-scale application of this method to produce made-to-order integral circuits[197] and for the repair of photo-stencils.[198] Possible developments of the method are: 1) an increase in the number of substances that can be deposited; 2) the development of new methods for obtaining particles of relatively complex shape, for example tubes, beakers, springs, etc.; 3) the production of assemblies for obtaining coatings on planar surfaces with an area greater than 100 cm^2, and also on non-planar objects (spheres, rods, tubes, etc.); 4) the discovery of new methods for controlling the structure of the material being deposited; 5) the improvement of deposition methods to increase the uniformity of the properties of the products and the reproducibility of the results; and 6) the extension of theories of the mechanism of deposition and the modelling of specific processes.

VII. Summary

The main progress in the study of laser-induced chemical processes has been made in the decomposition of gaseous hydrides, organometallic compounds, and carbonyls. Two types of process, photolytic and pyrolytic, are developing rapidly, and to some extent supplement one another.[199] Important advantages of pyrolytic processes are the short time and the local character of the heating of the support. This to some extent prevents irreversible thermal transformations (degradation, recrystallisation of the support, etc.), decreases the risk of the formation of undesirable powdered deposits, and also makes it possible to intensify mass exchange in the deposition zone. Most progress will apparently be made in photolytic reactions in the ultraviolet range, where it is possible to select photon energies sufficient for the rupture of chemical bonds.

An independent direction of research is the study of the intramolecular selectivity of deposition processes, achieved, for example, by the two-stage infrared–ultraviolet dissociation of molecules.[200] Promising possibilities are provided by the use of extremely short (femtosecond) laser pulses[201] and multi-wave laser radiation with a mixture of inert gas halides.[202]

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Current state of the problem of aromaticity

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ABSTRACT. The different aspects of the current concept of aromaticity, which is based on the advances in the synthesis of aromatic systems and a study of their properties by experimental physical techniques and theoretical quantum-mechanical methods, are examined. Magnetic, structural, and energy properties, but not reactivity, can serve as criteria of aromaticity as characteristics of the electronic structure of cyclic conjugated systems, stabilisation of which is due to a cyclic delocalisation of electrons. A wider interpretation on which ideas about multiple types of aromaticity are based is unjustified and unsuitable.

Contents

I.	Introduction	116
II.	Progress in the synthesis of aromatic systems	116
III.	Criteria of aromaticity	119
IV.	Aromaticity and reactivity	125
V.	The concept of aromaticity	126
VI.	Types of aromaticity	127

I. Introduction

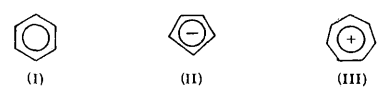
The problem of aromaticity is one of the principal problems in organic chemistry. More than 130 years since the Kekulé structure of benzene was established, it is undergoing a fruitful development through the close interaction between experiment and theory.[1–10] In the area of aromatic compounds, to which about 30% of all known organic products belong,[11] many fundamental rules of structure and reactivity have been established for the first time. During the time that the problem of aromaticity has been studied, theoretical organic chemistry has attained its most important achievements, such as the well-known Hückel rule, and at this point it has confronted a crisis, which has arisen from the proposal that the concept of aromaticity should be rejected altogether.[12–15]

The current state of the problem of aromaticity is very ambiguous. On the one hand, running in parallel to the development of the practical chemistry of aromatic compounds, the experimental and theoretical principles of aromaticity continue to be improved and extended. On the other hand, objections to aromaticity are discussed as before and all the time new types and variants of aromaticity are proposed, as a rule not being compatible with this concept. The main objects to aromaticity, which were put forward in the 1970s, are that aromaticity is not a physical quantity that could be measured directly[12] and the concept of aromaticity does not have a single meaning, as it comprises a number of postulates and theories.[13,14] The questions: "Aromaticity—myth or reality?",[14] "Aromaticity—an exercise in chemical nonsense?",[15] "Aromaticity not in fashion?",[16] "Aromaticity—theory or myth?",[17] became the titles or topics of publications, and the abundant forms of aromaticity became the subject of jokes ("schizoaromaticity"[12]). Even in studies that defended the usefulness of the concept of aromaticity,[6,10,16] together with wideness and universality, its diffuseness, physical heterogeneity, and the impossibility of a more or less rigorous determination are emphasised.

The erosion of the concept, the multiplicity of the types of aromaticity, the lack of a common view of the criteria for aromaticity, in particular the possibility of using reactivity as a criterion, have created certain complications in the chemistry of aromatic compounds. The present review aims to analyse the recent advances in the experimental and theoretical principles of aromaticity, to discuss the resulting concept of aromaticity, and to consider the ideas about the different types of aromaticity in this context.

II. Progress in the synthesis of aromatic systems

An accumulation of data from physical methods that constitute the foundation on which the concept of aromaticity is based has proved possible mainly as a result of the synthesis of different aromatic systems. During the early period of development of ideas about aromaticity[18] chemists did not even suspect that these systems existed. The modern era of the problem of aromaticity was started in 1931–1938 when Hückel developed the molecular orbital (MO) method to represent the electronic structure of unsaturated hydrocarbons, which led to the Hückel rule ($4n + 2$, $n = 0, 1, 2$, etc.) for determining the number of π-electrons with which a monocyclic, conjugated, planar carbopolyene is aromatic. Up to that time, benzene (I) and the cyclopentadienyl anion (II) as well as their heteroanalogues (pyridine, pyrrole, thiophene, etc.) were known as aromatic systems. Hückel attributed the aromaticity of benzene and the cyclopentadienyl anion to the completeness of the electron shell, in which six π-electrons completely occupied all three bonding orbitals, and he predicted the aromaticity of the cycloheptatrienyl cation (III). The synthesis of cycloheptatrienyl (tropylium) bromide in 1954[19] was the first step in a series of significant advances confirming the predictive power of the Hückel rule.



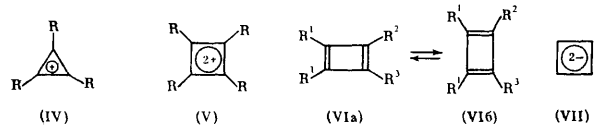
(I) (II) (III)

During the following years monocyclic, conjugated, neutral and charged polyenes were synthesised with the number of atoms (N) in the ring ranging from 3 to 30 ([N]annulenes); out of these the planar systems containing $4n + 2$ π-electrons were classed as aromatic,

while those containing $4n$ π-electrons were classed as antiaromatic. Many new polycyclic and heterocyclic aromatic systems were also obtained. It is useful within the scope of the present review to describe briefly a selection of the main products, studies on which led to elaboration of criteria and the development of the theory of aromaticity.

Systems containing 2π-electrons are known—the cyclopropenium cation (IV) and cyclobutadienyl dication (V). Salts of cyclopropenium[20] and its trialkyl-, triaryl-, and tricyclopropyl-substituted derivatives are stable, so they can be isolated in a crystalline state. Tetramethyl and tetraphenyl derivatives of dication (V) have been synthesised in a superacid medium at a low temperature and have been characterised from their NMR spectra.[21]

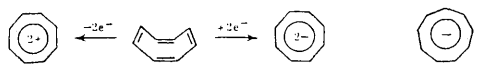
Cyclobutadiene (VI)[22] is the simplest antiaromatic system;[23] it has only been detected in an argon matrix during low-temperature photolysis (20 K). Cyclobutadiene derivatives stabilised by substituents such as t-butyl groups have been isolated in a pure form. A study of tri-t-butylcyclobutadiene using NMR spectroscopy[24] and generation of 1,2-dideuterocyclobutadiene with trapping of the isomers by dienophile[25] suggest that there is an equilibrium between the valence isomers (VIa) and (VIb), which, according to the NMR data, cannot be "frozen out" even at −185 °C.



(IV) (V) (VIa) (VIb) (VII)

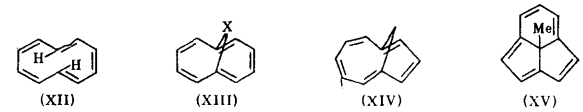
Despite the presence of 6π-electrons, the dicyclobutadienyl dianion (VII) does not possess aromaticity because of destabilisation resulting from interelectron repulsion in the small ring.[26,27]

Apart from benzene (I), the cyclopentadienyl anion (II), and the tropylium cation (III), the cyclooctatetraenyl dication (VIII) also belongs to the group of 6π-electron aromatic systems. The 1,3,5,7-tetramethyl-, tetraphenyl-, and 1,4-dimethyl-substituted derivatives of the latter are obtained when cyclooctatetraene (IX) is treated with SbF_5 at −78 °C.[28,29] When cyclooctatetraene (IX) is reduced with an alkali metal, it is converted to the cyclooctatetraenyl dianion (X)—a 10π-electron aromatic system.[30] The aromatic cyclononatetraenyl anion (XI) also has a 10π-electron shell.[31,32] In contrast to ions (VIII) and (X), cyclooctatetraene itself[33] is a typical cycloolefin; its non-planar molecule with $4n$ π-electrons ($n = 2$) has a boat conformation



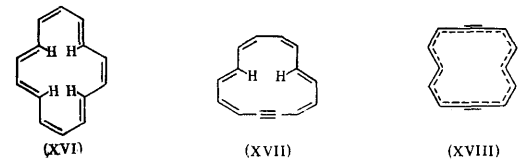
(VIII) (IX) (X) (XI)

Neutral monocyclic [10]annulenes[34] do not exhibit aromatic properties because of steric hindrance. Completely *cis*- and mono-*trans*-stereoisomers of [10]annulene have been isolated in a crystalline state at −80 °C, but they decompose when the temperature is increased. Despite the attempts undertaken, stereoisomer (XII) has not been prepared, since it is destabilised by the mutual repulsion of the hydrogen atoms at the 1- and 6-positions. Replacement of these hydrogen atoms by a bridging group (X = CH_2, CO, O, NH) leads to stable aromatic bridged 1,6-X-[10]annulenes (XIII) with a periphery as in naphthalene.[35–37] 1,5-Methano[10]annulene (XIV), with a periphery as in azulene, has also been synthesised.[38,39] Another type of bridged [10]annulene is the methano[10]annulene (XV) (7*b*-methyl-7*bH*-cyclopent[*cd*]indene).[40]



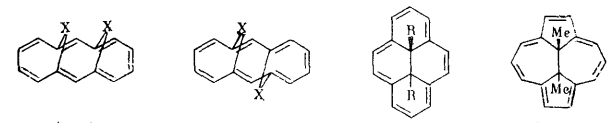
(XII) (XIII) (XIV) (XV)

In [14]annulene (XVI), just as in [10]annulene (XII) but to a lesser degree, there is overlap of the inner hydrogen atoms, and so compound (XVI) has comparatively low stability.[41] The overlap can be eliminated by the introduction of one (XVII) or two (XVIII) triple bonds with a change to dehydroannulenes.[42]



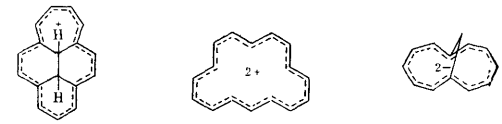
(XVI) (XVII) (XVIII)

Many bridged *syn*-1,6:8,13-bis-X-[14]annulenes (XIX) with a periphery as in anthracene, where X = CH_3, CO, CF_2, O, NH or X,X = $CH(CH_2)_nCH$ when $n = 0-3$, i.e. the bridges are joined together, have been synthesised. In contrast to the aromatic *syn*-isomers (XIX), the *anti*-isomers (XX) are extremely labile, reactive olefins. While *syn*-dioxo[14]annulene (XIX), X = CO, withstands flash pyrolysis at 500 °C, the corresponding *anti*-isomer (XX) must be kept in an atmosphere of argon at −40 °C. Another widely investigated group of bridged [14]annulenes is made up by 15,16-dihydropyrene compounds (XXI),[43] to which the bridged [14]annulene (XXII) (dicyclopenta[*ef*,*kl*]heptalene) is related.[44]



(XIX) (XX) (XXI) (XXII)

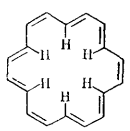
Aromatic ions containing 14π-electrons in the ring are known.[4,5] These are the bridge [15]annulenyl cation (XXIII), the [16]annulenyl dication (XXIV), the bridged 1,7-methano[12]annulenyl dianion (XXV), and others.

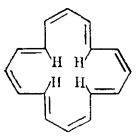


(XXIII) (XXIV) (XXV)

[18]Annulene (XXVI)—an example of aromatic systems with 18π-electrons—was historically the first macrocyclic annulene to be synthesised.[41] With its large ring size, the inner protons do not shield each other. The compound is relatively stable, it withstands distillation under reduced pressure, and can undergo aromatic substitution. Examples of bridged [18]annulenes are hexahydrocoronene which contains a central hydrogenated ring[45] and [18]annulene oxides, which contain the bonds of furan rings as a macrocycle.[46] Ions with 18π-electrons—the [17]annulenyl anion and [16]annulenyl dianion—have been reported. From among the higher annulenes with $4n + 2$ π-electrons, [22]annulene, a

[30]annulene derivative, and bisdehydro[22]-, bisdehydro[26]-, and bisdehydro[30]-annulenes have been synthesised. From among macrocyclic systems with $4n$ π-electrons, the extremely unstable [12]annulene and bridged [12]annulenes are known. [16]Annulene (XXVII), [20]annulene, and [24]annulene have been isolated in a crystalline state as have the corresponding bisdehydroannulenes. The monocations of the bridged [13]annulene and [15]annulene, the dianion of [18]annulene, and some others[4,5] have been detected spectroscopically.


(XXVI)


(XXVII)

The Hückel rule, strictly applicably only to monocyclic conjugated polyenes, has been extended to polycyclic compounds with the assumption, which has no theoretical basis, that the π system is determined by the periphery while the "inner" bonds and atoms do not introduce any significant perturbations (see, for example, the study of Rabinovich et al.[47]). Naphthalene (XXVIII) and azulene (XXIX) are aromatic bicyclic systems with 10π-electrons that have been thoroughly studied. The pentalene dianion (XXX) and bicyclo[6.2.0]-decapentaene (XXXI) [48] belong to the same group of 10π-electron systems. Bicyclic aromatic annulenoannulenes with one and three common bonds between the macrocycles,[49] such as a structure consisting of two rings of bisdehydro[14]annulene (XVIII), have been synthesised.


(XXVIII)

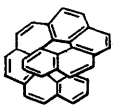

(XXIX)

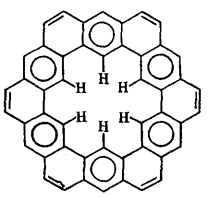

(XXX)


(XXXI)

The variety of polycyclic aromatic hydrocarbons is created through linear, angular, and peri-annelation to bicyclic structures. Linear benzannelation leads from naphthalene to anthracene, tetracene, pentacene, etc; angular benzannelation leads to phenanthrene and then to helicenes, which are hydrocarbons with their molecules in the form of cylindrical spirals, such as in octahelicene (XXXVI), since the spatial overlap of the rings makes a planar structure impossible. They have spiral asymmetry which is a special case of chirality. Helicenes containing 13 and 14 rings twisted into three coils of a single spiral have been synthesised.[50]

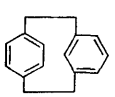
Polycyclic hydrocarbons that are built up from annelated benzene rings forming a closed loop have the group name of corannulenes.[51] The simplest example of a corannulene, for which the name was originally proposed, is the sterically strained hydrocarbon composed of five benzene rings with a pentahedron in the centre. Coronene and kekulene (XXXIII) which on the inside have a periphery of [6]- and [18]-annulene and on the outside have a periphery of [18]- and [30]-annulene respectively, belong to this group. The synthesis and study of the properties of kekulene (XXXIII) [52] and a theoretical analysis[51,53] have led to the conclusion that the electronic system of corannulenes consists of benzenoid rings with a sextet of π-electrons (XXXIIIa) rather than two electronic systems of annulenes (XXXIIIb).

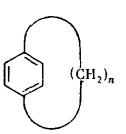

(XXXII)


(XXXIIIa) (XXXIIIb)

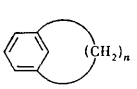
The Hückel rule is not applicable to polycyclic peri-annelated structures that have atoms common to the three rings if all of the π-electrons are taken into account. The phenalenium cation, pyrene, and perylene are examples of peri-annelated aromatic systems with the total number of electrons being $4n$ but with $4n + 2$ π-electrons around the periphery.

Polycyclic non-condensed hydrocarbons in which the benzene rings are joined together by polymethylene chains in a ring are classed as cyclophanes.[54] For two benzene rings, three series of [m,n]cyclophanes are possible: para–para, meta–meta, and meta–para, when $m,n \geqslant 2$, for example, [2,2]metaparacyclophane (XXXIV). The benzene rings can be joined by three chains at the 1-, 3- and 5-positions, and also arranged in several layers when one ring simultaneously forms two loops. [n]Cyclophanes in which the polymethylene chain links the para- (XXXV) or meta- (XXXVI) positions of a single ring are also known. Cyclophanes with the shortest chain, in which the benzene ring is substantially bent, are of interest for studying the relationship between aromaticity and coplanarity (Section III).


(XXXIV)



(XXXV)



(XXXVI)

A whole series of heteroaromatic compounds can formally be derived from carbocyclic compounds by replacing a single CH group with a heteroatom Y that can supply one electron to the aromatic π-system or by replacing two adjacent CH groups with a heteroatom X that can supply a pair of electrons. The replacement of one or more CH groups in benzene by a heteroatom Y results in a six-membered aromatic heterocycle, and replacement of two adjacent CH groups in benzene or, from another viewpoint, replacement of a CH^- group in the cyclopentadienyl anion by a heteroatom X leads to five-membered aromatic heterocycles. Replacement of a CH^+ group in a cationic aromatic system by a heteroatom from Group III can result in the conversion to a neutral heteroaromatic molecule, for example, going from the tropylium cation to borepine.

A similar conversion is possible in other [$4n + 2$]annulenes and in polycyclic compounds. Among 10π-electron heteroaromatic systems, there have been reports on heteronines (XXXVII),[55] which are isoelectronic to the cyclononatetraenyl anion (XI) and from amongst which azonine (X = NH) is thermally stable to 50 °C and oxanine (X = O) is unstable, and on diheteronines (XXXVIII),[56] which are isoelectronic to the cyclooctatetraene dianion (X). Stable bridged aza analogues of 1,6-methano[10]annulene (XIII) with a quinoline and isoquinoline periphery and monoazoanalogues of [14]annulene (XVI) and [18]annulene (XXVI) [36,57] have been synthesised.

Dihydroporphins (around a ring that contains pyridine nitrogen atoms and excludes pyrrole nitrogen atoms) are regarded as 1,10-diaza[18]annulenes.[58]


(XXXVII)


(XXXVIII)


(XXXIX)


(XL)

In polycyclic heteroaromatic compounds, heteroatoms can simultaneously form part of two rings as in indolizine or the quinolizinium cation and in specific cases they can belong to three rings at the same time. Cyclazines,[57] which in view of the insignificant electronic interaction through the central atom can be regarded as analogues of bridged methenoannulenes, have a similar structure. Thus, [2.2.3]cyclazine (XXXIX) is analogous to the aromatic methenoannulene (XV), while [3.3.3]cyclazine (XL) is analogous to the antiaromatic [12]annulene. since in polycyclic compounds carbon atoms in different rings and different combinations can be replaced by heteroatoms, the number of known heterocyclic aromatic systems many times exceeds the number of carbocyclic systems.

III. Criteria of aromaticity

Of crucial significance is the question of choosing criteria which would make it possible to judge whether a given compound is aromatic and if possible to measure the degree of aromaticity. Properties of molecules that can be measured by experimental physical methods are used as criteria. These constitute magnetic and structural methods and data on the thermodynamic stability obtained mainly by calculation

1. Magnetic criteria

As the electronic system of organic compounds in the vast majority of cases does not have spherical symmetry, their magnetic susceptibility is anisotropic. In aromatic compounds this is reflected particularly clearly, since apart from the effect of local anisotropy caused by the electron shells of individual atoms, non-local anisotropy occurs, due to the combined system of π-electrons in the molecule, the so-called "ring current". The concept of the ring current is given by a postulated model,[59] the veracity of which has been confirmed by the agreement of the properties calculated using it and those measured experimentally. The use of magnetic criteria essentially consists of detecting magnetic properties non-local components, which would indicate the presence of a ring current.

The magnetic susceptibility on right-angled coordinates is expressed as the sum $\chi_M = 1/3(\chi_x + \chi_y + \chi_z)$. The essence of anisotropy of diamagnetic susceptibility is that the component along the axis perpendicular to the plane of the aromatic ring is always greater than that measured in the plane of the ring: $\chi_z \gg \chi_x \approx \chi_y$.

The difference between the components is a measure of the anisotropy:

$$\Delta\chi_M = \chi_z - 1/2(\chi_x + \chi_y).$$

Direct measurement of the anisotropy of molar diamagnetic susceptibility $\Delta\chi_M$ requires the growth of a monocrystal and an initial determination of the molecular orientation. Other methods are based on the Zeeman effect in microwave rotational spectra[60] and on a determination of deuteriated compounds in high-resolution ^{2}H NMR spectra.[61] Analysis shows[60,62] that only a fraction of $\Delta\chi_M$ (Table 1) for aromatic compounds, about a half for benzene,[60] can be attributed to the ring current, whereas the other fraction is due to local anisotropy. The experimental difficulties and the need to separate the contributions of the local and non-local components limit the widespread use of the anisotropy of diamagnetic susceptibility as a criterion of aromaticity.

Table 1. Anisotropy and exaltation of diamagnetic susceptibility (-10^{-6} cm^3 mol^{-1}).

Compound	$\Delta\chi_M$ (Ref.60)	χ_M (Ref.63)	$\chi_M - \chi_M^{loc}$	
			Λ **	χ_M^{nonloc}***
Benzene	59.7*; 62.7	54.8	13.7 (18.0)	12.5
Naphthalene	119.8*	91.9	30.5 (36)	—
Anthracene	182.4*	130.3	48.6 (55)	—
Phenanthrene	165.5*	127.9	46.2 (53.5)	—
Pyrene	222.4*	155	57	—
Azulene	—	91.0	29.6 (35.5)	—
Pyridine	57.2	49.2	13.4 (18.3)	9.1
Pyrrole	42.4	47.6	10.2 (14.5)	12.7
Furan	38.7	43.1	8.9 (13.9)	9.9
Thiophene	50.1	57.4	13.0 (17.8)	13.0
1,3-Cyclohexadiene	—	48.6	—0.7	—
[16]Annulene	—	105	—5	—

* Determination using the monocrystal orientation method; the remaining figures were obtained using microwave spectroscopy.

** Using the Haberditzl increments[63] to calculate χ_M^{loc}; in brackets — using Pascal constants, taken from Ingold[64] for hydrocarbons and from Pozharskii[9] for heterocycles.

*** Using Hameka parameters[65] to calculate χ_M^{loc}.

A property which is simpler to determine is the difference between the total molar magnetic susceptibility of an aromatic compound and that of an analogous hypothetical compound with localised bonds $\chi_M - \chi_M^{loc}$, known as the exaltation of diamagnetic susceptibility (Λ) [63] or non-local magnetic susceptibility (χ_M^{nonloc}).[65] The total magnetic susceptibility χ_M of the compound under study is measured experimentally by determining the force at which the sample of the substance is repelled by a magnetic field of given strength. The magnetic susceptibility of the hypothetical compound with localised bonds χ_M^{loc} is calculated as the sum of the contributions of the separate structural elements of the molecule. It is clear from the examples in Table 1 that the exaltation of diamagnetic susceptibility Λ is negative and considerable in absolute value, for the non-aromatic 1,3-cyclohexadiene it is equal to zero, and for the antiaromatic [16]annulene (XXVII) it is opposite in magnitude. It should be mentioned that, based on some of the same experimental values of χ_M, different values of Λ or χ_M^{nonloc} are given in the literature depending on which parameters are used in the calculation of χ_M^{loc} (see Table 1). A relationship between the non-local components of the diamagnetic susceptibility, its axial component, and the anisotropy has been deduced: $3\chi^{nonloc} = \chi_z^{nonloc} = \Delta\chi^{nonloc}$.[65] The index based on the anisotropy of optical polarisability[66] is similar to the exaltation of diamagnetic

susceptibility. The index based on the Faraday effect—the enhancement of the rotation of the plane of polarised light by a sample of an aromatic compound placed in a magnetic field compared to the rotation for the hypothetical model with localised bonds calculated from increments[14]—is also related to the magnetic susceptibility.

The comparative simplicity of determination and the applicability to different classes of compounds make the enhancement of diamagnetic susceptibility a practicable index for aromaticity. Its weak point lies in the need to calculate the diamagnetic susceptibility of hypothetical compounds by an additive scheme, which always holds the chance of errors, especially since anomalies are found for real compounds. Thus, for cycloheptatriene and cyclopentadiene values are obtained which would class them as aromatic compounds (Λ = 8.1 and 6.5 respectively).[63,65]

The simplest method to use in the study of aromaticity, requiring moreover a minimal quantity of substance, is the determination of chemical shifts of the protons in an aromatic ring in ^{1}H NMR spectra. As a result of the ring currents which generate an anisotropic diamagnetic field in aromatic compounds, inside the ring directed against the external magnetic field and outside the ring lying along the line of the external magnetic field, the signals from protons positioned inside the ring or above it are displaced upfield, while the signals from protons lying in the plane of the ring on the outer side are displaced downfield (diatropy). In antiaromatic compounds a paramagnetic field occurs, so that the signals from the inner protons are displaced downfield and the signals from the outer protons are displaced upfield (paratropy).

The difference between diatropic aromatic and paratropic antiaromatic systems is shown most clearly in a series of annulenes, where the recording of the chemicals shifts of protons has served as an important instrument in the classification of aromaticity, confirming the validity of the Hückel rule. The difference between the chemical shifts of the outer and inner protons in the ^{1}H NMR spectra of neutral aromatic [4n + 2]annulenes is 7–12 p.p.m., in the spectrum of the aromatic [16]annulenyl dianion it is about 16 p.p.m.[4] For antiaromatic annulenes this difference has a reverse sign and amounts to 2–7 p.p.m., while for the antiaromatic [18]annulenyl dianion it is about 30 p.p.m. The greater difference for the anions reflects the phenomenon, which has a theoretical basis,[67] that in charged aromatic–antiaromatic systems the ring current is greater than in neutral systems. In a series of diatropic tetra-t-butyl-substituted bisdehydro[N]annulenes containing t-butyl groups at the α-positions relative to the triple bonds, the difference between the chemical shifts of the outer and inner protons, taken as a measure of the ring current, decreases from 13.8 p.p.m. when N = 14 (XVI) to 4.0 p.p.m. when N = 30.[42] The fact that in the ^{1}H NMR spectrum of kekulene (XXXIII) the signal from the six inner protons occurs downfield at 8.37 p.p.m. and not far upfield as in [18]annulene has served as evidence for the benzenoid structure of (XXXIIIa) [52] (see Section II).

In bridged [4n + 2]annulenes the chemical shifts of the protons situated above the plane of the ring are strongly displaced upfield. For example, in 1,6-methanol[10]annulene (XIII), X = CH_2, the protons of the CH_2 group resonate at −0.51 p.p.m. while the ring protons resonate at 6.95–7.27 p.p.m.[41] Reduction of *trans*-15,16-dimethyl-15,16-dihydropyrene (XXI), R = Me, to the dianion, with a change from a 14π-electron aromatic system to a 16π-electron antiaromatic system causes the chemical shifts of the protons of the methyl group to change from −4.25 to 21.0 p.p.m. and the ring protons to change from 8.14–8.65 to −3.2 to −4.0 p.p.m.[41]

The vast majority of aromatic compounds contain medium or small rings which have only outer electrons. Their chemical shifts have to be compared with the chemical shifts of protons in model compounds rather than those of inner protons. In the case of benzene, for example, the signal in its spectrum is displaced 1.5 p.p.m. downfield relative to the signals from the olefinic protons of 1,3-cyclohexadiene, which can be selected as a model. It would appear to be possible to estimate the strength of the ring current from the degree of displacement of the signals, and hence estimate the degree of aromaticity. The ready availability of ^{1}H NMR spectra and the apparent simplicity in interpretation have given rise to many attempts of this type. Their failure has generally been because only a part of the chemical shift can correctly be related to the ring current. It is also necessary to take into account the contribution of the effect of local anisotropy and the influence of the distribution of electron density. An analysis applied to polycyclic benzenoid hydrocarbons[68] shows that only 50% or less of the total magnitude of the chemical shift can be attributed to the delocalisation effect, while the remaining proportion is defined as the contribution from local anisotropy. A simple comparison of the values of the chemical shifts of protons cannot give a true picture of the ratio of ring currents and is more suitable for establishing aromaticity than quantifying it.

The displacement of the signals in ^{13}C NMR spectra when a ring current occurs are approximately the same in absolute magnitude as in proton spectra, but since the range of chemical shifts of ^{13}C NMR is an order higher than for ^{1}H nuclei, the relative changes in chemical shifts in ^{13}C NMR spectra are small and are readily masked by other effects.[69]

From among the indices of aromaticity in use that are based on the measurements of chemical shifts, mention should also be made of "displacement by dilution" and "displacement from the solvent". The first of these is the displacement of a signal in the ^{1}H NMR spectrum when a liquid aromatic compound is diluted with an inert non-polar solvent multiplied by the molar volume: $\Delta\delta.V_M$. Referral of this value to the analogous one for benzene gives an index expressed in percent.[8] "Displacement from the solvent" is the difference between the chemical shifts of a polar molecule (acetonitrile) and a non-polar molecule (cyclohexane) in the liquid aromatic compound under study. It has been shown[70] that this parameter does not measure the ring current or aromaticity.

2. Structural criteria

A geometric characteristic of the molecules of aromatic compounds is their tendency to form a coplanar configuration of the atoms and bonds of equal length in the aromatic ring. Current methods for establishing the molecular structure—X-ray and neutron diffraction analysis, gas-phase electron diffraction analysis and microwave spectroscopy of free molecules—make the geometric parameters of almost all aromatic systems possible to determine.

The tendency towards coplanarity is due to the advantage of colinearity of the axes of the p orbitals for their effective overlap. An important question concerns what deviation from a planar configuration is admissible without a loss of aromaticity. A study of sterically strained aromatic compounds such as helicenes, corannulenes, and particularly cyclophanes with short bridges, provides data about this. The benzene ring in [n]paracyclophanes (XXXV) is distorted into the form of a boat with a deviation of 15–17° from planarity when n = 7,[54] 20–21° when n = 6 [71] (X-ray diffraction data), 22–24° when n = 5 (data from calculations).[72] In one derivative[5] of metacyclophane (XXXVI),

n = 5, one side of the boat is deflected by 27° and the other by 12°.[73] Despite this, the bonds in the benzene ring of these compounds are of equal length, and the values of the bond lengths and chemical shifts in the ^{1}H NMR spectra lie in the usual region for aromatic compounds. A determination of the anisotropy of diamagnetic susceptibility using high-resolution ^{2}H NMR for 8,11-dideutero[5]metacyclophane confirms that the ring is aromatic.[74] Calculations on the molecules of [5]paracyclophane [72] and [6]paracyclophane [75] using non-empirical quantum-chemical methods suggest that there is considerable destabilisation due to strain in the distorted benzene ring.

In unstrained aromatic systems the deviations from planarity that occur are usually small. From the data for strained structures and quantum-chemical calculations the view was expressed that even unstrained aromatic rings are flexible in the ground state when the deviations from planarity range from 5–20°.[76] An analysis of the vectors of the π-orbital axes in the case of bridged [10]annulenes (XIII)–(XV) shows that the molecule has a tendency to bend in order that the overlap of the π-orbitals should be at a maximum.[77]

The stability of a planar geometry of the system as determined by calculating the change in energy on bending about one of the axes has been proposed as a theoretical conformational criterion of aromaticity or antiaromaticity.[78] Systems in which the change to a non-planar conformation gives rise to a large endothermic change, a large exothermic change, or a small change in energy are classed as aromatic, antiaromatic, or non-aromatic respectively. It was found using a non-empirical MO method (6–21 G basis) that for aromatic benzene, pyridine, and pyrazine bending along the 1–4 axis by 20° requires energies of 62.8, 37.7, and 33.5 kJ mol^{-1}, while for the non-aromatic 1,4-dihydropyrazine the energy required is −9.2 kJ mol^{-1}. According to this criterion the system of the cyclobutadienyl dication (V), R = H, Me, for which non-empirical calculations[27,29] show that a non-planar conformation folded along a diagonal by about 35°, for example, when R = H, with an energy barrier of 19 kJ mol^{-1} (4–31 G basis) should be classed as non-aromatic. From the data on the distortion of a planar structure of the ring in strained aromatic molecules and the absence of a direct relationship between acoplanarity and antiaromaticity[10] it follows that the degree of planarity is not in itself sufficient as a criterion.

The carbon–carbon bond lengths in aromatic compounds have values that are intermediate between the length of a single C_{sp^2}–C_{sp^2} bond [(1.465 Å in butadiene)[80]] and a C=C double bond (1.337 Å in ethylene[80]). There is a clear difference between aromatic and antiaromatic compounds in the distribution of bonds. Thus, in the planar molecule of the aromatic [18]annulene (XXVI) there is no alternation in bonds: the 12 inner bonds have a length of 1.38 Å and the 6 outer bonds have a length of 1.42 Å, whereas in the conformationally mobile molecule of the antiaromatic [16]annulene (XXVII) single (1.44–1.47 Å) and double (1.31–1.35 Å) bonds alternate.[4]

According to the data from all known methods the benzene molecule has D_{6h} symmetry with equal bonds (1.397 Å). Despite this, the view has recently been expressed that even in this case a structure with D_{3h} symmetry and alternating bonds cannot be excluded because of the possibility of a molecular configuration with a 30° bend in crystals and the averaging out when gas-phase methods are used.[81] This point of view raises objections, particularly on the grounds that according to quantum-chemical calculations using a non-empirical method (3–21 G* basis) a structure with D_{3h} symmetry does not correspond to a minimum on the potential energy surface and has appreciably inferior stability compared to a D_{6h} structure.[82]

In a few other aromatic systems the bond lengths are also equal, according to X-ray diffraction data. For example, in the triphenylcyclopropenium cation (IV), R = Ph, they are 1.373 Å,[83] and in the cyclooctatetraenyl dianion (X) they are 1.407 Å.[84] However, a complete uniformity of bonds is rather more than the exception. In the vast majority of carbocyclic aromatic compounds, not to mention heterocyclic compounds, the C–C bond lengths are not fully equivalent. Introduction of substituents or annelation into the benzene ring disrupts the complete uniformity of the bonds. In napthalene (XXVIII) the C_α–C_β bonds are reduced to 1.371 Å, and the remaining bonds are increased to 1.412–1.422 Å;[80] in phenanthrene the C(9)–C(10) bond length is only 1.350 Å while the C(10)–C(10a) bond is elongated to 1.453 Å.[85]

The lengths of the bonds involving heteroatoms in heteroaromatic compounds vary over a wide range. Structural studies of the hetero analogues of benzene with Group V elements indicate that as its number in the Periodic Table increases, the angle in the ring at the heteroatom decreases while the length of the carbon–heteroatom bond increases, constituting 117° and 1.37 Å in pyridine, 101° and 1.73 Å in phosphabenzene (phosphorine), 97° and 1.85 Å in arsabenzene, and 93° and 2.04 Å in stibabenzene.[86] The stability of the compounds decrease in the same series. However, all molecules remain planar with C–C bond lengths equalled out to 1.38–1.41 Å, which suggests that there is a retention of aromaticity, which is weakened by an unfavourable geometry.

It has been proposed through the introduction of special indices that the degree of equivalence of the bond lengths in the ring should be used as a quantitative characteristic of aromaticity. The index of Julg[87] constitutes the product of two factors:

$$A = A_1 \cdot A_2 = [1 - 225/n\Sigma (1 - d_{rs}/\bar{d})^2] \cdot \Pi [1 - (\Delta q_{ij}/d_{ij})^2].$$

The first term strictly represents the degree of equivalence of n C–C bonds in the ring, having length d between atoms r and s with average length $\bar{d}$. This factor is not very sensitive to the variation in bond lengths: benzene 1.00, naphthalene 0.90, azulene 1.00, pyrrole 0.91. Therefore a second factor is introduced, taking into account the difference in the π-charges Δq_{ij} on the neighbouring atoms. The introduction of a corrective factor which operates with the magnitudes of charges calculated by a quantum-chemical method has the result that index A loses its purely experimental basis. Critical comments have been made and the opinion has been expressed that the Julg index is unsatisfactory.[9,88,89]

An index has been built up from an analysis of the bond lengths obtained experimentally or calculated by a quantum-chemical method. This index is based on the so-called "harmonic oscillator model of aromatic stabilisation" (HOMAS):[90]

$$I(\mathrm{HOMAS}) = 1 - \frac{98.89}{n} \sum_{r=1}^{n} (d_{\mathrm{opt}} - d_r)^2.$$

Calculation and summation of the squares of the differences are carried out separately for each type of bond using the optimum value of the length (d_{opt}): C–C 1.397, C–N 1.338, N–N 1.308, C–O 1.300 Å. When applied to polycyclic compounds, this index is more convenient for characterising the aromaticity of individual rings.[90]

Since a direct comparison of the lengths of bonds involving different atoms is impossible, a conversion from the experimental values of the bond lengths (d) to their orders (N) is used by calculation from the correlative equation: $N = ad^{-2} - b$, where a and b are empirical constants (for values, see the studies of Pozharskii[9] and Bird[91]). The problem then essentially consists of developing an index which reflects the variation in the bond orders. Pozharskii[9] proposed the index $\Delta\overline{N}$, which is the average value of the variations of the orders of n bonds, including single bonds, calculated as the sum of all the differences ΔN divided by their quantity, which is equal to the number of sets of n to the power 2: $\Delta\overline{N} = \Sigma\Delta N/C_n^2$. In order to express the aromaticity in percent, the aromaticity of benzene ($\Delta\overline{N} = 0$) is taken as 100% and that of cyclopentadiene ($\Delta\overline{N} = 0.49$) is taken as 0%, which gives a scale relative to the factor $I = 100(1 - \Delta\overline{N}/0.49)\%$.

On the same basis, Bird[91-93] introduced a similar scale, in which the variation of the bond orders is given by the ratio of the mean square deviation to the arithmetic mean of the bond orders:

$$V = \frac{100}{N}\sqrt{\Sigma(N - \overline{N})^2/n}.$$

For the aromaticity scale, the aromaticity of a completely delocalised system ($V = 0$) was taken as 100% and the index of the corresponding Kekulé structure with completely localised bonds ($V_K = 35$ for five-membered rings, $V_K = 33.5$ for six-membered rings) was taken as 0%; $I = 100(1 - V/V_K)\%$ (Table 2).

Table 2. Structural indices of aromaticity.

Compound	Aromaticity, %		Compound	Aromaticity, %	
	(Ref.9)	(Refs.91, 92)		(Ref.9)	(Refs.91, 92)
Benzene	100	100	Pyridine	82	85.7
Naphthalene	63	—	Pyridazine	65	78.9
Thiophene	45	66	Pyrimidine	67	84.3
Pyrrole	37	59	Pyrazine	75	88.8
Selenophene	37	59	1,2,3-Triazine	65	76.9
Tellurophene	20	48	1,2,4-Triazine	71	86.1
Furan	12	43	1,3,5-Triazine	100	100
Phosphole	8	35	1,2,4,5-Tetrazine	88	97.8
Tetrazole	80	72	Pyridinium	54	66.7
1,2,4-Triazole	71	81	Pyrilium	28	65.8
Pyrazole	61	73	Phosphorine	61	74.1
Imidazole	43	64	Sydnone	17	42
Thiazole	43	64	2-Pyridone	22	59

The structural indices are based on experimental results, they effectively differentiate the aromaticity of compounds, they provide a single continuous scale, and in the case of polycyclic compounds they can be used to determine both the system as a whole and its separate cyclic fragments. Inapplicability to symmetric systems is among their limitations. In comparing the two variants of structural index it is clear that the distribution of compounds in terms of aromaticity is on the whole similar, although the ratios of aromaticities in a number of cases do not agree, sometimes by a substantial amount. Thus, according to the Pozharskii index, furan is 8 times and phosphole is 12 times less aromatic than benzene, whereas according to the Bird index they are only respectively 2.3 and 2.8 times less aromatic. On the first scale 1,2,4-triazole is less aromatic than tetrazole, on the second scale it is the reverse. Since both indices are based on the same collection of data and only differ according to the way these are treated mathematically, qualitative discrepancies cannot be justified. The development of a common approach is required.

Jug[94] has proposed that the least of the complete ($\pi + \sigma$) bond orders of the system, calculated by one of the semiempirical MO methods (SINDOl) with optimisation of geometry, should be taken as a criterion of aromaticity and called the ring current index. Examination of the values given reveals a number of discrepancies with the results of experimental criteria. Thus, pyrazole proves to be a non-aromatic compound and furan is more aromatic than pyrazole as well as imidazole (cf. Table 2).

Information about the degree of fixation of the bonds in an aromatic ring can be obtained from the values of spin-spin coupling constants of vicinal protons ($^3J_{HH}$) in ^{1}H NMR spectra. The $^3J_{HH}$ constants when other conditions are equal show a linear dependence on the length (order) of the C–C bond and are larger the shorter the length (higher order) of the bond.[69] When the bonds are exactly the same length as in benzene, the ratio of constants of the neighbouring bonds $J_{rel} = 1$, when there is complete localisation of single and double bonds as in 1,3-cyclohexadiene or compound (XLI) $J_{rel} \approx 0.5$. In bicyclic aromatic compounds J_{rel} has intermediate values; in naphthalene, for example, $J_{12}/J_{23} = 0.82$.[95] As the vicinal spin-spin coupling constants depend not only on the length of the C–C bond but also on the C–C–H bond angles in planar systems, which are different in five- and six-membered systems, and on the electronegativity of the heteroatoms and substituents present in a molecule, this index has limited use. It is only suitable when comparing compounds that are similar in structure, such as the benzoheterocycles (XLII) and (XLIII), which formally have a benzenoid and orthoquinoid structure, and the values of the constants $J_{rel} = J_{45}/J_{56}$ vary from 0.89 to 0.93 and 0.70 to 0.74 respectively.



(XLI)



(XLII)



(XLIII)

X = NR, O, S

3. Energy criteria

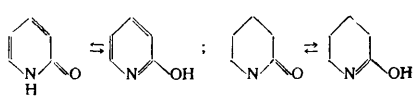
The opportunity for aromatic systems to exist arises because cyclic declocalisation of the π-electrons leads to an increase in thermodynamic stability of the molecule, namely, to a decrease in the level of its internal energy. A gain in energy is a necessary condition of aromaticity and could serve as a sufficient criterion if there were reliable methods of determining it. The difficulty in using energy criteria occurs precisely because of the inadequacy of these methods. The principal difficulty is that the energy of a real aromatic molecule has to be compared with the energy of a hypothetical molecule with non-interacting localised double and single bonds. The difference between the energies of these structures, which is known as the resonance energy (RE), cannot be completely determined on an experimental basis since the reference structure does not exist in reality. Therefore the resonance energy as the principal energy criterion of aromaticity is either determined by combining experiment with calculation (empirical RE) or calculated theoretically using quantum-mechanical methods.

The empirical resonance energy (ERE) is determined as the difference between the heat of combustion or heat of hydrogenation of an aromatic compound determined experimentally and the corresponding value for a model structure calculated by an additive scheme as the sum of the contributions of individual bonds.

$$E(\text{ERE}) = -(\Delta H^{\text{exp}} - \Delta H^{\text{addit}})$$

(The minus sign indicates that the resonance energies of aromatic systems are defined as positive). A determination of the ERE from the heat of hydrogenation is preferred if hydrogenation is practicable, as it constitutes the difference between not such large numbers as in a determination from the heat of atomisation. The main source of uncertainty arises not because of errors in the thermodynamic experiment but in the complexity of including all the factors in calculating the heats of atomisation or hydrogenation of the model compound. In particular, there is no single method for determining the energy of a single $C_{sp^2}-C_{sp^2}$ bond in structures without conjugation. Depending on whether averaged bond contributions or bond contributions that take into account the environment are used in the calculation of the heat of combustion of 1,3,5-cyclohexatriene, the ERE value of benzene varies from 0.5 to 3 eV (see Ref. 3, p. 19). The ERE values of some compounds, determined from heats of combustion, are given below in Table 3. Attempts to deduce rational numerical values of the bond contributions based on a critical analysis of thermochemical data by compromises and assumptions do not improve the situation very much.[96]

An experimental study of reversible chemical reactions—acid–base, tautomeric, and redox reactions—can give some idea of the magnitude of the stabilisation energy. Thus, the equilibrium constants that corresponds to formation of aromatic ions clearly indicate their stabilisation. This is suggested by the high acidity of cyclopentadiene, which is deprotonated to the aromatic cyclopentadienyl anion (II) (pK_a = 15 [5]) compared to the acidity of alkanes, for example (pK_a = 68–70 [97]); the high basicity of the ketones—cyclopropenone, tropone, and phenalenone (pK_a = −3.1, −0.6, −1.4 respectively[98])—protonation of which leads to the formation of the hydroxy derivatives of the aromatic cyclopropenium (IV), tropylium (III), and phenalenium cations, compared to the basicity of acetone, for example (pK_a = −7.2); and the values of the equilibrium constants (pK_{R^+}) of the reaction: $R^+ + H_2O \leftrightarrows ROH + H^+$, for aromatic cations such as tricyclopropylcyclopropenium (IV), R = C_3H_5, (pK_{R^+} = 10.0)[99] one of the most stable carbocations, tropylium (III) (pK_{R^+} = 4.7),[100] the bridged cation of [15]annulene (XXIII) (pK_{R^+} > 8.7),[5] etc. compared to a stabilised conjugated cation such as Ph_3C^+ (pK_{R^+} = −6.4).[100] From a comparison of two reversible reactions, one of which involves aromatic compounds and the other involves non-aromatic compounds, these being similar in structure, the ERE difference between the aromatic tautomers can be determined. Thus, a comparison of the constants of the tautomeric equilibrium of the aromatic compounds 2-pyridone (XLIVa) ⇆ 2-hydroxypyridine (XLIVb) with the corresponding hydrogenated models (XLVa) ⇆ (XLVb) shows that the ERE of 2-hydroxypyridine is 0.32 ± 0.04 eV greater than that of 2-pyridone.[8]



(XLIVa) (XLIVb) (XLVa) (XLVb)

In determining the empirical resonance energy, the reference structure, the energy of which is calculated by summation of the bond contributions derived from data for alkanes and alkenes, is a model with alternating bonds, namely, with a geometry that differs from the geometry of the aromatic molecule which has equalised bonds. The resonance energy relative to the reference structure with the same geometry is known as the vertical resonance energy. It is greater than the ERE by an amount equal to the distortion energy that is necessary to stretch the double bonds and compress the single bonds. The deformation energy on going from cyclohexatriene to benzene is estimated at 1.17–1.60 eV while the vertical resonance energy is estimated at 2.73–4.83 eV.[101]

Since the total stabilisation energy of the system depends on its size, in order to compare different systems resonance energy values calculated for one π-electron are used. Standardisation of the resonance energy on the basis of one atom [102] and one bond [103] and the ratio of the resonance energy to the complete π-electron energy of the reference structure (% RE) have also been proposed.[104]

In the Hückel approximation the quantity which should correspond to the vertical resonance energy is the delocalisation energy (DE). It constitutes the difference between the π energy of the system calculated by the Hückel MO method and the π energy of double bonds represented as a Kekulé structure. The contribution of each of the latter is equated with the π-energy of an ethylene molecule (2β). Since benzene has a π-energy equal to 8β as calculated by the Hückel MO method while cyclohexatriene has a π-energy of three ethylene molecules, equal to 6β, the delocalisation energy of benzene is 2β. The delocalisation energy values of certain other hydrocarbons are given in Table 3. It is to be expected from the delocalisation energy values that all the annulenes except for cyclobutadiene, not only those that satisfy the Hückel rule but also benzocyclobutadiene or pentalene, which do not exist in a free state, should be aromatic. With respect to its resonance energy value per π-electron (Table 3) benzene is below the polycyclic hydrocarbons, and the lower polyacenes fall below the higher members, which is at variance with the actual data on the stability and properties of these compounds.

By taking into account the unsuitability of the resonance energy as a criterion of aromaticity and the rought approximation that have to be resorted to in calculating the energies of hypothetical cyclic polyenes as reference compounds, Dewar proposed that they should be replaced by acyclic polyenes with an open chain.[105] This introduced a fundamental improvement in the calculation of resonance energy. In a determination of the Dewar resonance energy (DRE), the Pariser–Parr–Pople SCF MO method is used to calculate the heats of atomisation of the cyclic compound under study, and in order to calculate the heat of atomisation of the reference structure the energies of the double and single bonds, which in a series of polyenes are given by the constants:

$$E(\text{DRE}) = -(\Delta H^{\text{cycl}} - \Delta H^{\text{acyl}}).$$

are added up. Relating this to the number of π-electrons in the system gives the Dewar resonance energy per π-electron, denoted by the acronym REPE (resonance energy per electron). This parameter (Table 3) is in much better agreement with the actual material. Its value is highest for benzene, it decreases on going from lower polyenes to higher polyenes, it is close to zero for pentalene, and for cyclobutadiene it acquires a negative value. When thermochemical data are available for acyclic polyenes, the Dewar resonance energy can be calculated from them with the same results reached as in the

calculation of the heats of atomisation of acyclic polyenes by summation of the bond energies.[106] The Dewar resonance energy (DRE) is less than the empirical resonance energy (ERE) by an amount equal to the conjugation energy in the acyclic polyene, which may be expressed in terms of the conjugation energy (CE) of butadiene:[107]

$$E(\text{DRE}) = E(\text{ERE}) - nE(\text{CE}) \text{ (butadiene)},$$

where n is the number of single bonds in the reference structure.

With the development of quantum chemistry it became possible to calculate the resonance energy on an entirely theoretical basis using a non-empirical method. The quantum-mechanical vertical resonance energy for benzene, obtained by a non-empirical MO method (DZ basis) which takes into account electron correlation, is 3.34 eV; the distortion energy is 1.30 eV; the adiabatic resonance energy, which is equivalent to the empirical resonance energy, is 2.17 eV; and the standardised energy, which is equivalent to the Dewar resonance energy calculated from the equation above, is 1.00 eV when the conjugation energy of butadiene is 0.39 eV.[107]

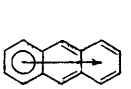
By formulating a new theoretical criterion of aromaticity, Dewar rejected at the same time hypothetic cyclopolyenes as reference models and the Hückel MO method for the calculation of energies, having expressed the view that it was unsuitable for further use in organic chemistry.[105] It transpired, however, that the main point was not the change in method of calculation but the exchange of models. Hess and Schaad showed[106,107] that in a correlation of the π-energy of a conjugated cyclic system calculated by the Hückel MO method with the π-energy of the corresponding acyclic polyene obtained by an additive method, agreement with the actual data is just as satisfactory as when using a SCF MO method (Table 3). In order to calculate the energy of an acyclic polyene in a determination of the resonance energy by the Hess–Schaad method (HSRE), the empirical parameters required for the bond energies are not of two types but eight types, depending not only on the multiplicity of the bond but also the number and position of the hydrogen atoms.[112,116]

A way of calculating the resonance energy within the scope of the Hückel MO method has been developed[114,115] with the use of graph theory techniques. In the Hückel MO method the complete π-energy of the molecule is expressed as the sum of the molecular orbital energies, taking into account how they are filled. The problem essentially consists of determining the coefficients of the characteristic polynomial, the roots of which constitute the orbital energies (in β units). By using a topological scheme based on the graph-theory theorem of Sachs, it is possible to calculate the polynomial coefficients directly from the molecular structural formula (molecular graph). The coefficients are calculated by summation of the total number of components of the molecular graph, taking into account the cyclic component. If the contribution of the cyclic component in the coefficients is omitted, a polynomial that corresponds as if to the same system but without the ring will be obtained. Summation of the roots of this polynomial, known as acyclic, gives the reference energy, which is subtracted from the π-energy of the conjugated system to give the topological resonance energy (TRE):[114,115]

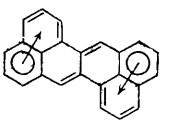
$$E(\text{TRE}) = \sum_{i=1}^{n} g_i(x_i - x_i^{ac}),$$

where x_i and x_i^{ac} are the roots of the cyclic and acyclic polynomial and g_i is the degree of occupation of the π-orbitals by electrons (Table 3). While in a determination of the Dewar resonance energy and Hess–Schaad resonance energy the reference energy belongs to an acyclic polyene represented by a structural formula, in the determination of the topological resonance energy it has only a mathematical representation as an acyclic polynomial. Because of this, the topological resonance energy is applicable not only to neutral carbocyclic and heterocyclic molecules for which Kekulé structures can be drawn but also to ions, radicals, excited states, and unusual combinations of atoms.

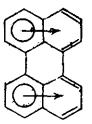
In addition to calculations of the resonance energy based on SCF MO and Hückel MO methods, several methods have been proposed for calculating the resonance energy of carbocyclic benzenoid systems with empirical parametrisation, having similar features to the valence method and based on the sextet structures of Clar,[117] Kekulé structures,[108] or "conjugated" rings,[118] revealed in the molecular structure. Clar introduced a circle as a distinctive symbol of a sextet of π-electrons for those rings in polycyclic hydrocarbons which, as in the Kekulé structure of benzene, have three double bonds; this made it possible to make a qualitative interpretation of many properties.[119,120] Apart from sextets in the molecule there are rings which are capable of "diluting" the sextet through transfer of two π-electrons to them, which is shown by an arrow as in anthracene (XLIV), rings with fixed double bonds as in cetrene (XLV), or "empty" rings like the central ring in perylene (XLVI). It is assumed that the more aromatic a compound is, the more sextets there are in its structure and the less the sextets are "diluted" through the participation of neighbouring rings.



(XLIV)



(XLV)



(XLVI)

In order to make a quantitative determination of the resonance energy of a polycyclic benzenoid hydrocarbon, all of the Clar structures are written out and the number of sextets, isolated double bonds, and rings "diluting" an adjacent sextet are determined in each, the numbers are added up, and after that, by using numerical values of these parameters (in eV), the resonance energy is calculated from a linear equation.[117] The values of the parameters are defined from an empirical correlation with the Dewar resonance energy. This method is also suitable for characterising the local aromaticity of individual rings. In a similar manner, a calculation is carried out on the basis of Kekulé structures[108] or conjugated rings,[118] when each ring in each Kekulé structure is examined and evaluated by type. Theoretical analysis suggests that there is an inherent similarity between the different methods for calculating the resonance energy.[116]

All variants of the resonance energy which are calculated using an acyclic polyene as the reference structure are resonance energies in the Dewar sense. By using this theoretical index of aromaticity it is possible to trace the border between aromatic, antiaromatic, and non-aromatic compounds, depending on whether the resonance energy is positive, negative, or close to zero, and also to develop a continuous scale of aromaticity as the resonance energy per π-electron increases. Comparison of the three variants of the scale—DRE, HSRE, and TRE (Table 3)—shows that on the whole they agree non-linearly, although they have particular differences or

discrepancies. Thus, according to the value of the Dewar resonance energy, benzocyclobutadiene is aromatic, to a greater degree that azulene and furan, while pentalene is non-aromatic. On the other hand, according to the values of the Hess–Schaad and topological resonance energies, benzocyclobutadiene and pentalene are anti-aromatic. Attention is drawn to the fact that on the latter two scales, where the resonance energies of ions are calculated, it is not benzene that occupies the first place with respect to aromaticity, but separated by a large amount is the cyclopropenium cation, followed by the cyclopentadienyl anion and the tropylium cation. According to its Hass–Schaad resonance energy value per π-electron (-0.002β),[102] the cyclobutadienyl dication is classed as a non-aromatic system, which is consistent with the data of the conformational criterion (see Section III). The relative positions on the different scales for compounds that are similar in structure do not always coincide. For example, on the DRE and TRE scales pyrimidine is more aromatic than pyrazine while on the HSRE scale their aromaticity is the same, whereas according to the data of structural criteria (Table 2) pyrazine is more aromatic than pyrimidine.

Table 3. Resonance energy values.

Compound	*E*(ERE), eV (Refs.8, 101)	calculated per π-electron			
		E(RE), β (Refs.99,108)	*E*(DRE), eV (Refs.105, 109–111)	*E*(HSRE), β (Refs.102, 112, 113)	*E*(TRE), β (Refs.114, 115)
Benzene	1.56	0.333	0.145	0.065	0.046
Naphthalene	2.64	0.368	0.132	0.055	0.039
Anthracene	3.62	0.380	0.114	0.047	0.034
Phenanthrene	3.96	0.389	0.138	0.055	0.039
Tetracene	4.77	0.385	0.101	0.042	0.031
Pentacene	—	0.388	0.091	0.038	0.029
Pyrene	4.72	0.407	0.131	0.051	0.037
Perylene	5.48	0.412	0.131	0.048	0.037
Azulene	1.30	0.336	0.017	0.023	0.015
Cyclobutadiene	—	0.000	−0.193	−0.268	−0.307
Benzocyclobutadiene	—	0.298	0.054	−0.027	−0.049
Pentalene	—	0.307	0.001	−0.018	−0.026
Cyclopropenium cation	—	—	—	0.365	0.268
Cyclopentadienyl anion	—	—	—	0.111	0.094
Tropylium cation	—	—	—	0.108	0.032
Pyridine	1.00	—	0.151	0.058	0.038
Pyrimidine	—	—	0.146	0.049	0.032
Pyrazine	—	—	0.106	0.049	0.022
Pyrrole	0.92	—	0.038	0.039	0.040
Furan	0.68	—	0.031	0.007	0.007
Thiophene	1.24	—	0.047	0.032	0.033
Quinoline	2.05	—	0.142	0.052	0.036
Isoquinoline	—	—	0.142	0.051	0.033
Indole	2.04	—	0.103	0.047	0.038
Isoindole	—	—	0.050	0.029	0.032
Carbazole	3.21	—	0.127	0.051	—

It should be noted that the conclusions about aromaticity that are based on the value of the resonance energy depend to a considerable extent on the quantum-chemical calculation method being used, particularly in borderline cases. An obvious example of this is the controversy over the nature of the electronic system of bicyclo[6.2.0]decapentaene (XXXI).[48] The system was predicted to be antiaromatic using the simple Hückel MO method and other methods, and at the same time from graph theory it was concluded to be diatropic,[121] which could have fundamental importance as a refutation of the obligatory interrelationship between diatropy and aromaticity. On the other hand, a non-empirical method gave an indication that it was weakly aromatic $E(\mathrm{RE}) = 0.17$ eV,[122] which is in better agreement with the conclusions from the experimental data (NMR, X-ray diffraction, thermochemical).[48] In order to avoid similar situations, it is advisable on the basis of calculations that only those systems with a large absolute value of the resonance energy should be termed aromatic (antiaromatic).[123]

The essential significance of the theoretical methods lies in their identification of the nature of aromatic stabilisation and establishing its relationship with magnetic and structural properties used as experimental criteria. The determination of a quantitative relationship between the resonance energy and the magnetic parameters of a molecule is regarded[59] as a considerable success. A simple ratio has been derived, relating the resonance energy to the ring current (K) and the non-local diamagnetic susceptibility resulting from it for [N]annulenes with $4n + 2$ π-electrons:[124,125]

$$E(\mathrm{RE}) = -\frac{\pi^2}{mS}K, \tag{1}$$

$$E(\mathrm{RE}) = -\mathrm{const}\,\frac{\chi^{\mathrm{nonloc}}}{S^2}, \tag{1'}$$

where S is the area of the ring (for benzene S is assumed to be 1), $m = 3$ [125] or $m = 4$,[126] $\mathrm{const} = -\frac{1}{8m}\left(\frac{hc}{e}\right)^2$. . The sign of the ring current indicating its direction, which is opposite in sign to the resonance energy, denotes that diatropy is a necessary attribute of aromaticity.[104] From equation (1) it is possible to develop a linear correlation between the ratio of the difference in chemical shifts ($\Delta\delta$) of the outer and inner protons in neutral aromatic [N]annulenes (see Table 2) to the area of the ring and the value of E(RE) per π-electron:[126]

$$\Delta\delta/S = k.E(\mathrm{RE})/\mathrm{N}, \tag{2}$$

where k is a proportionality coefficient. The relationship established between the resonance energy and the ring current, which shows that delocalisation of the bonding π-electrons in the ring serves as a common origin of both aromatic stabilisation and diamagnetic exaltation, provides a theoretical basis for using experimental magnetic criteria.

It was concluded from statistical treatment of the numerical values of 12 different indices of aromaticity for 15 heterocycles and benzene using the main characteristics that the structural criteria I and ΔN and the energy criterion DRE on the one hand and the magnetic criteria χ_M and Λ on the other hand are mutually orthogonal, constituting the scales of two types of aromaticity—"classical" and "magnetic".[89] The remaining indices occupy an intermediate position. No opinions are put forward about the physical nature of the orthogonality, even though this conclusion clearly contradicts the relationships in equations (1) and (2). It cannot be excluded that this is not related to the fundamental difference between the scales but to a deficiency in determining the numerical values of the magnetic characteristics χ_M and Λ, especially for heterocycles (see Section III).

IV. Aromaticity and reactivity

For a long time reactivity was the main criterion of aromaticity. A year after the publication by Kekulé on the structure of benzene and about aromatic compounds being structurally similar to

benzene, the idea was put forward by Eilenmeyer about the chemical similarity of aromatic compounds.[18] Since electrophilic substitution reactions are typical for benzene, it was the capacity for these reactions that was considered, and in a number of studies up to the present time has been considered, to be a sign of aromaticity. The tendency of aromatic compounds to undergo substitution rather than addition reactions, the tendency to "retain their form" is due to their increased thermodynamic stability, namely, to a reduced level of free energy. However, the reactivity depends not only on the level of the free energy of the ground state of the substrate but is determined by the difference between the levels of the ground and transition states—the free energy of activation. The energy of the transition state varies in general over such a wide range that the variation of the upper limit of the activation barrier can completely mask the effect of a change in the lower limit, which depends on the degree of aromaticity.

This is clearly illustrated by an examination of the following series of aromatic compounds: sodium cyclopentadienide, pyrrole, benzene, pyridine, tropylium bromide. The cyclopentadienyl anion undergoes electrophilic substitution extremely readily; on going to pyrrole and then benzene and pyridine the ease of electrophilic substitution is decreased, and up to now it has not been possible to involve the tropylium cation in any electrophilic reaction. On the other hand, tropylium salts react very readily with various nucleophilic reagents, pyridine undergoes these reactions with more difficulty, benzene reacts with great difficulty, and sodium cyclopentadienide does not react at all. In this series the reactivity towards electrophilic reagents decreases on going from the cyclopentadienyl anion. The same applies to the ease of nucleophilic nucleophilic reagents it is in the reverse order without any apparent relationship to the degree of aromaticity. The reason for the lack of correlation between the reactivity and aromaticity in this case is precisely because the energy of activation changes mainly as a result of the reduction or increase in the energy level of the transition state. The nature of this change is clear in terms of the collision theory. It is obvious that the repulsion forces which the converging particles have to overcome are incomparably greater when the particles have the same charge as in electrophilic attack on a tropylium cation that when they have different charges as in electrophilic attack on a cyclopentadienyl anion. The same applies to the ease of nucleophilic attack on a tropylium cation and its difficulty in the case of a cyclopentadienyl anion. The same applies to the ease of nucleophilic the π-deficient heterocycle of pyridine occupy respective intermediate positions between ions and benzene.

Even under ideal conditions for comparing compounds—with the reagent standardised, a common mechanism, the absence or levelling out of solvation, catalytic, and other effects—the reactivity depends directly on the degree of aromaticity only when the energy level of the transition state remains constant. In practice, these conditions cannot usually be achieved. Therefore reactivity cannot in general serve as a criterion of aromaticity. Only in a series of compounds that are similar in structure, when the changes in energy of the transition state and ground state are proportionate, there is a linear correlation between the changes in resonance energy and the free energy of activation, as for example in the case of the Diels–Alder reaction of aromatic hydrocarbons with maleic anhydride.[127] Moreover, the tendency for "preservation of form" is typical not only for aromatic but also for certain non-aromatic conjugated systems. On the strength of this, Lloyd and Marshall[13,128] proposed that aromatic and non-aromatic compounds that exhibit this tendency should be combined into the same group, having given them the new name "meneidic", and the term "aromatic" should be rejected, but they did not meet with support.

There is a fundamental and complex interdependence between reactivity and aromaticity rather than a simple relationship. The electronic structure of the substrate not only determines the lower level of the activation barrier but also has an effect on the structure of the transition state and intermediates. Information about aromaticity is not sufficient but entirely necessary for an understanding of reactivity. However paradoxical are the general features of reactivity, which cannot serve as a criterion of aromaticity but are extremely important in the practical sense, the main concern is what binds together the chemistry of aromatic compounds and prompts its separation into an independent branch of organic chemistry.

V. The concept of aromaticity

The accumulated facts and interrelationships suggest that cyclic conjugated molecules or ions have common structural features which are responsible for their stabilisation, and they are known as aromatic. The means of representing the electronic structure depends on the chosen method. When applying the MO method, which is that most widely used at the present time, the movement of electrons in delocalised orbitals is the topic under discussion, for the model with localised orbitals, their overlap (spin interaction) is being considered.[129]

Thus, the concept of aromaticity applies to molecules whose structural features serve to combine atoms into a ring and conjugation in the ring is "an alternating sequence (in the structural formula) of single and double bonds."[130] In ions this sequence is augmented with a cation or anion site. The physical scope of aromaticity in terms of the MO method is cyclic delocalisation of electrons causing a gain in energy, which stabilises the system.

Aromaticity is a special property of electron shells, and the latter cannot be observed directly. Therefore the objection to aromaticity on the grounds that it cannot be measured directly is unjust.[12] In reality aromaticity is exhibited in magnetic, structural, energy, and magnetic properties. If the phenomenon is not confused with its effect on properties, another objection to aromaticity, namely, that aromaticity is a combination of different ideas[13,14] is eliminated.

The present concept of aromaticity does not leave room for the ideas about different types of aromaticity that appear in the literature. In the vast majority of cases these ideas are based on a different, wider interpretation of aromaticity, where all distinguishing features apart from stabilisation of the system, including the occurrence of cyclic delocalisation or electrons and the ring itself, may be omitted as non-essential, and conjugation is taken to mean "overlap of the atomic *p* orbitals of three or more neighbouring atoms"[130] rather than an alternating sequence of bonds. The variety of types of aromaticity strengthens the position of critics of the concept, since if there are many "aromaticities", it may not as such exist. It is useful to examine the terms that have been introduced to denote the types of aromaticity, responding to two questions in each case: whether the type of stabilisation which is implied by the term introduced has been demonstrated, and if so, to what extent can it be justified to call this type of stabilisation aromatic.

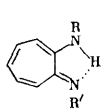
VI. Types of aromaticity

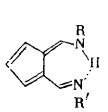
In the literature there are about 20 terms that are formed by adding a prefix or adjective to the word "aromaticity". Some of them only stress the degree of aromaticity (arch-, super-aromaticity)[14,53] or constitute abbreviations (heteroaromaticity,[9] perfluoroaromaticity[16]). Antiaromaticity (non-aromaticity) is the opposite of aromaticity and is an inherent part of the concept. Conjugated cyclic systems in which cyclic delocalisation of electrons leads to destabilisation are considered to be antiaromatic.[23] The remaining terms put forward to denote the types of aromaticity can be divided into three categories: those arising from the basic concept of aromaticity given above; those based on a wider interpretation of it; those related to an extension of the concept of aromaticity.

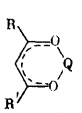
1. Ideas arising from the basic concept of aromaticity (pseudo-, non-classical, quasi-, homo-aromaticity)

Pseudoaromaticity. This term arose from the empirical rule of Craig for dividing conjugated mono- and poly-cyclic structures into aromatic and pseudoaromatic according to their formal symmetry sign in valency schemes.[131] The latter category contained those structures from which stabilisation could not be expected as a result of cyclic delocalisation of π-electrons, including all monocyclic molecules with $4n$ π-electrons starting with cyclobutadiene. Thus the concept of pseudoaromaticity in this sense completely duplicates the more contemporary concept of antiaromaticity. Moreover, single attempts were made to use the term pseudoaromaticity (and pseudoantiaromaticity) in a discussion of the *p*-orbital interactions in non-aromatic species—the cyclopropyl cation and anion,[132] and unsaturated diradicals.[133]

Non-classical aromaticity and quasiaromaticity. The terms non-classical aromaticity[134] and quasiaromaticity[135] have been put forward to represent the aromaticity of conjugated compounds with intramolecular hydrogen bonding (IHB), while quasiaromaticity has also been proposed for the aromaticity of metal chelates.[136] In these structures cyclic delocalisation of the π-electrons in a chelate ring involving vacant $2p$ orbitals of the hydrogen atom or *d* orbitals of the metal atom was proposed. For example, in compounds (XLVII) and (XLVIII) an aromatic 10π-electron system as in azulene has been proposed, with a symmetrical configuration of the hydrogen atom equidistant from the heteroatoms (when R = R′ = Ph), which would appear to be confirmed by the nature of the NMR spectra and the X-ray diffraction data. However, subsequent studies showed that this was an illusion created by the rapid prototropic tautomerism and the statistical distribution of tautomers in crystals. The asymmetric configuration of the hydrogen atom in IHB in compounds (XLVII) was demonstrated by spin-lattice relaxation,[137] and low-temperature ^{1}H NMR spectroscopy was used to demonstrate the existence of tautomers in compounds (XLVIII),[138] which excludes delocalisation via IHB, which would cause the stabilisation of a single form with equivalent bonds.


(XLVII)


(XLVIII)

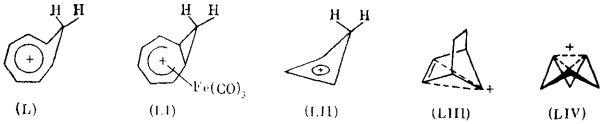

(XLIX)

The ^{1}H NMR spectra of acetylacetonates (XLIX) do not provide any evidence of a ring current.[139,140] The displacement of the signals downfield is satisfactorily shown to be due to a redistribution of positive charge of both metal chelates and borochelates, although in the latter cyclic delocalisation is impossible since the tetrahedral boron atom does not have any vacant low-lying orbitals for the formation of π-bonds.[139] Hence the π-electron system in conjugated compounds with IHB and metal chelates is acyclic in nature. Lloyd and Marshall[141] suggested that the scope of the term "quasi-aromatic" should be changed and applied to non-aromatic compounds that are similar to aromatic compounds in the tendency to "retain their form", but shortly afterwards they rejected their proposal.[13] Recently this recommendation was put foward again.[123]

Homoaromaticity. The concept of homoaromaticity was put forward by Winstein in 1959 in relation to cyclic structures in which the sequence of conjugated bonds is interrupted one or more times by a methylene group with an sp^3-hybridised carbon atom. It was suggested that cyclic delocalisation of electrons may be preserved in this case because of overlap of the atomic *p* orbitals of non-bonded carbon atoms of a type intermediate between π- and σ-overlap. Mono-, bis-, and tris-homoaromaticity has been proposed in a very large number of structures, both neutral and charged (see reviews[142–144]), but homoaromaticity can only be regarded as firmly established in certain cations.

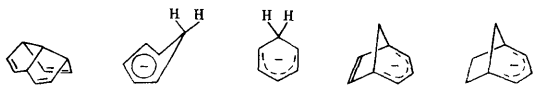
The clearest example of monohomoaromaticity is the homotropylium cation (L), which is formed by the action of strong acids on cyclooctatetraene. Arguments in favour of the homoaromaticity of cation (L) were obtained from ^{1}H NMR spectra and X-ray diffraction data.[144] In the NMR spectra the signals from the protons of the methylene group differ markedly; the signal from the exocyclic proton occurs at 5.86 p.p.m. and that from the endocyclic proton is at −0.73 p.p.m. Such an unusual upfield shift of the latter signal for carbocations has been attributed to the effect of a ring current in the seven-membered residue, having a sextet of π-electrons. X-Ray diffraction analysis of 2-hydroxyhomotropylium hexachloroantimonate shows that the seven-membered residue has the conformation of a shallow boat, and the methylene group deviates from the average plane of this by approximately 90 degrees. The C(1)–C(7) distance of 1.626 Å suggests that there is a bonding interaction and at the same time excludes the alternative structure of a bicyclo[5.1.0]octadienyl cation. This type of bicyclic structure is exhibited by the ligand in a complex with iron tricarbonyl (LI), where the chemical shifts of the protons of the CH_2 group are almost the same (1.53 and 1.35 p.p.m.) while the C(1)–C(7) bond length in the fluoroborate is 1.474 Å.[144] A theoretical study of the structure of cation (L) reveals a minimum on the potential energy surface when the C(1)–C(7) bond length is 1.7–2.0 Å and the occurrence of a ring current.[145]

From among the other well studied homoaromatic cations, the cyclobutenyl (homocyclopropenium) (LII), 7-norbornenyl (bishomocyclopropenium) (LIII), and cyclohexenyl (trihomocyclopropenium) cations (LIV) may be mentioned.[143]


(L) (LI) (LII) (LIII) (LIV)

In neutral molecules, as was recognised in the result of detailed experimental and quantum-chemical studies, homoaromatic stabilisation is absent,[146,147] and the corresponding structures are even destabilised through repulsion between the filled orbitals. However, for the bridged trishomobenzene — triquinacene (LV) — by determining the heat of hydrogenation compared to the corresponding monoolefin, the stabilisation energy was found[148] to be E(ERE) = 0.19 eV, which would appear to require the question to be raised again.

Even more controversial is the question of homoaromaticity in anions. It was shown by means of NMR spectroscopy that the anions formed by deprotonation of 1,3- and 1,4-cyclohexadienes have the planar structure of the cyclohexadienyl anion (LVII) [149] rather than the structure of the homocyclopentadienyl anion (LVI). The main debate has revolved around the homoaromaticity of the bicyclo[3.2.1]octadienyl anion (LVIII). Deuterium exchange (DMSO/t-BuOK) in a hydrocarbon corresponding to anion (LVIII) occurs $10^{4.5}$ time faster than in its analogue without a double bond, corresponding to anion (LIX).[150] A determination of the acidity of the hydrocarbons in cyclohexylamine by treatment with caesium cyclohexylamide[151] and in the gas phase[152] shows that anion (LVIII) is more stable than anion (LIX) by 51 and 44 kJ mol^{-1} respectively. In the ^{1}H and ^{13}C NMR spectra of the anion the signals from the nuclei at the double bond in the 6- and 7-positions are displaced 2.3 p.p.m. (^{1}H) downfield and 43.8 p.p.m. (^{13}C) upfield compared to the spectrum of the conjugated acid, which suggests the delocalisation of negative charge involving the double bond.[153] The authors of the experimental studies regard these findings as proof of the bishomoaromaticity of anion (LVIII). However, it was concluded from quantum-chemical calculations carried out using semiempirical and non-empirical methods[154,155] that homoaromaticity does not play a substantial role in the stabilisation of anion (LVIII), which is attributed to the inductive effect of the double bond. Calculations by Brown et al.[156] led to the opposite conclusion, but a non-empirical calculation at a higher level[157] confirmed the absence of homoaromaticity. In order to account for the delocalisation of charge, the suggestion was made concerning salts of anion (LVIII) existing in solution as a contact ion pair in which the metal atom serves as a charge relay between the double bond and the anion site.[157] This hypothesis is supported by the agreement between the results of calculating the ion pair between the bicyclooctadienyl anion (LVIII) and lithium cation[158] and the X-ray diffraction data for the complex between lithium bicyclooctadienide and tetramethylethylenediamine.[159]



(LV) (LVI) (LVII) (LVIII) (LIX)

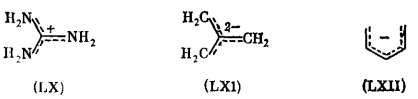
Thus in this group of examples only homoaromaticity relates to a proven structural form of aromaticity, characteristic of only a fairly limited group of carbocations.

2. Ideas arising from a wider interpretation of the concept of aromaticity (*Y*-, *U*-, bicyclic, spiro-, in-plane, double, trefoil, cruciform, metallo-, three-dimensional, and spherical aromaticity)

In accordance with a wider interpretation, the concept of aromaticity can be applied to various systems where there is stabilisation through orbital interactions. The forms of aromaticity differ from each other according to the manner of overlap of the atomic orbitals in the respective structures.

Y-Aromaticity. This is an application of the concept of aromaticity to a non-cyclic system. The term was introduced[160] to interpret the remarkable stability of the acyclic guanidinium cation (LX), as a result of which the basicity of guanidine (pK_a = 13.6) approaches that of the hydroxide anion. The stability of cation (LX) has been related to the completeness of its electron shell, which is formed by π-overlap of atomic p orbitals in which 6 electrons, as in the benzene molecule, are located in three bonding MOs, which gives rise to the analogy. This type of stabilisation has been proposed in other species with a *Y*-configuration,[160] in particular in the trimethylenemethane dianion (LXI).[161] However, dimetallation of 2-methyl-1,5-hexadiene does not give a substituted trimethylenemethane dianion.[162] Quantum-chemical calculations of the isolated dianion (LXI) and its derivatives indicate that D_{3h} symmetry is energetically preferred,[163,164] but in the crystalline state of the dilithium salt of the tribenzylidenemethane dianion an asymmetric structure occurs, with a geometry that is determined by the interaction with the counterions.[164] The stability of the guanidinium cation (LX) and similar heteroatomic structures is accounted for by the rule of topological stabilisation of charge[165] — the advantage in replacing carbon atoms by a more electronegative heteroatom at those positions where there is the highest electron density in the isoelectronic hydrocarbon. Stable ions with a *Y*-configuration are classified as quasiaromatic (see above), namely, they do not possess aromaticity but display a tendency to preserve their system of conjugation.[123]

U-Aromaticity. This term is used in relation to stabilisation of the *U*-conformation of 6π-electron anions of acyclic conjugated polyolefins — the 1,3-butadienyl dianion, 1,3,5-hextrienyl dianion, and pentadienyl anion (LXII) — through orbital interactions.[161]



(LX) (LXI) (LXII)

Bicycloaromaticity. The concept of bicycloaromaticity was introduced[166,167] in relation to bicyclic ions in which the charged site is formally included simultaneously in two bishomoaromatic rings with $4n + 2$ π-electrons, as in the 7-norbornadienyl cation (LXIII) or bicyclo[3.2.2]nonatrienyl anion (LXIV). It has been suggested that the orbital interaction between the two bishomoaromatic rings results in additional stabilisation through the formation of a single bicycloaromatic system. The fact that cation (LXIII) is stabilised relative to its saturated analogue (LXV) is not in doubt. Solvolysis of 7-X-norbornadiene (X = Cl, OTs), giving cation (LXIII), occurs 10^{14} times faster than the solvolysis of 7-X-norbornane, which is regarded as the "world record" for anchimeric assistance.[142] The question arises as to what proportion of the stabilisation energy is due to bishomoaromaticity and how much can be attributed to bicycloaromaticity. Comparison with the solvolysis of 7-*anti*-X-norbornene, which gives the bishomocyclopropenium cation (LIII), shows that introduction of one double bond increases the rate of solvolysis by a factor of 10^{11} while introduction of the second double bond with a conversion to cation (LXIII) increases it by a factor of 10^3.[168] Hence, the main role is played by bishomoaromaticity. Since in the 7-norbornadienyl cation (LXIII), where the

conditions for bicycloaromaticity are most favourable, the effect is small, there is no serious basis for expecting bicycloaromaticity in other cationic structures.[154,168] In order to interpret the effect of the bridging double bond in cations of the type (LXIII), which is one of a large number of cases of neighbouring group participation, it is quite unnecessary to resort to ideas of a special type of aromaticity. As far as anions of the type (LXIV) are concerned, the probable absence of homoaromatic stabilisation in anions (see above) eliminates the question of their bicycloaromaticity.



(LXIII) (LXIV) (LXV)

Spiroaromaticity. This has been suggested[169,170] in relation to the concept of spiroconjugation,[171] which is the stabilisation in unsaturated spiro compounds, such as in *spiro*-[4,4]nonatetraene (LXVI), through overlap of orthogonal *p* orbitals of the atoms of the double bonds adjacent to the nodal carbon atom. The consequence of spiroconjugation is a relative change in the HOMO and LUMO levels, so that experimental confirmation of the effect can be seen mainly in displacement of maxima in the electronic and photoelectronic spectra.[171] However, theoretical analysis using perturbational molecular orbital theory[172] leads to the conclusion that the total stabilisation due to spiroconjugation, called spiroaromaticity, is not significant in the molecule of (LXVI), and on increasing or decreasing the size of the rings becomes even less likely. The only case of appreciable stabilisation was predicted in *spiro*-[3.3]heptadienyl (LXVII) as a hypothetical non-classical species.[172]



(LXVI) (LXVII)

In-plane (radial), double, and trefoil aromaticity. All these variants of aromaticity assume that a cyclopolyene is stabilised through overlap of the radially positioned *p* orbitals lying in the plane of the ring. A group of compounds in which in-plane (radial) aromaticity[147] can be visualised is made up by [*n*]pericyclynes, which are cyclic hydrocarbons with a skeleton made up of *n* acetylene residues alternating with CH_2 groups. In pericyclynes the interaction between *p* orbitals lying in orthogonal planes has been studied theoretically.[173,174] The best conditions for in-plane orbital interaction exist in the first member of the series—the so far unknown [3]pericyclyne (LXVIII). Overlap of the orbitals in its molecule could be expected to lead to the formation of two 6π-electron systems—trishomoaromatic and in-plane. However, a quantum-chemical calculation (MNDO method) shows that [3]pericyclyne (LXVIII) is less stable by 2.63 eV than its valence isomer, tricyclopropanebenzene (LXIX).[174] In decamethyl-[5]pericyclyne the empirical resonance energy has been determined thermochemically as being of the order of 0.34 eV, attributed to homoconjugation[175] rather than in-plane conjugation. As a result of the calculation (MNDO) of about 100 different three-dimensional structures in which radial overlap could be expected, only in one of the isomers of dodecahedropentaene was a stabilisation energy of the order of 0.35 eV recorded.[147]



(LXVIII) (LXIX) (LXX)

The term "double aromaticity" was applied[176] to the 3,5-dehydrophenyl cation (LXX), the structure of which is assigned to the $C_6H_3^+$ ion in the mass spectrum. In cation (LXX), in addition to a sextet of π-electrons, a three-centre, two-electron bond inside the ring has been postulated, which provided a basis for suggesting aromaticity in orthogonal planes or double aromaticity.

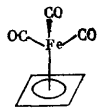
The idea of such a three-centre, two-electron bond in annulenes with $4n + 2$ π-electrons on the periphery has been put forward as a new type of aromaticity—trefoil aromaticity—and the respective structures as a potentially new class of aromatic molecules for which a new name has been proposed—trefoilenes, for example, [5.5.5]trefoilene (LXXI).[177] However, calculations have so far not confirmed the energy preference of the trefoilene configuration in any single model.[147] In all cases the valence isomers have proved much more stable; for example, the so far unknown trisallene (LXXII) is more stable by 4.3 eV than the hypothetical [5.5.5]trefoilene (LXXI).[178] According to calculations,[179] structure (LXXI) is only possible as a transition state of the degenerate isomerisation of a bicyclic carbene.



(LXXI) (LXXII) (LXXIII)

Cruciaromaticity. This has been put forward[180] to denote the orbital interaction in planar complexes of unsaturated ligands with transition metals such as iron in (LXXIII), where intersection of two π-systems occurs as a result of the participation in them of d_{xz} and d_{yz} metal orbitals, the plane of which form a cross on the surface.

Metallo- and three-dimensional aromaticity. A considerable advance in organometallic chemistry was the synthesis of a complex between the antiaromatic cyclobutadiene molecule and iron tricarbonyl $C_4H_4Fe(CO)_3$, which proved to be a stable compound that underwent electrophilic substitution without decomposition. A large number of complexes of cyclobutadiene with other metals have been prepared (see reviews[181,182]). According to X-ray diffraction data the $C_4H_4Fe(CO)_3$ complex is in the form of a bipyramid (LXXIV), at the base of which is a square with a side of 1.44 Å and at the apex is an iron atom with an Fe–C distance of 2.05 Å. Quantum-chemical calculation using a non-empirical method[183] shows that the C_4H_4Fe residue has 6 electrons in three bonding orbitals which are formed by effective overlap of the cyclobutadiene orbitals (e_g) with d_π orbitals of iron that have a similar level of energy. The C_4H_4–Fe bond is largely covalent. On the whole the molecule can be represented as the C_4H_4Fe metalloaromatic fragment perturbed as bonding with carbonyls. In contrast to compounds (LXXIV), complexes of transition metals with benzene and the cyclopentadienyl anion having the general formula (LXXV) should more accurately be regarded as systems of benzene and the cyclopentadienyl anion perturbed by bonding with the metal[183] rather than metalloaromatic systems.



(LXXIV)



(LXXV)



(LXXVI)

Complexes with the general formula (LXXV), where X above the annulene ring at the apex of the pyramid is not necessarily a transition metal atom but may also be an atom of an element from the first period (Li, Be, B, C, N), have been assigned[184] to a special type of three-dimensional aromatic system where there is a complete electron shell with $4n + 2$ π-electrons, regardless of whether the bonding of the X-link is a decisive factor. In this case, for example, the unstable complex π-complex of benzene with the Li^+ cation (LXXVI) is classed as an example of three-dimensional aromaticity on a level with the cyclobutadiene complex (LXXIV). More justified is the approach[183] in which the weak interactions are regarded as an excitation of the planar aromatic system. Pyramidal structures of the type (LXXV) and other three-dimensional non-classical structures have been successfully represented without involving the concept of aromaticity.

Spherical aromaticity. When the surface of a graphite disk is evaporated using a laser beam, among the products is detected a stable C_{60} cluster,[186] for which the structure of a truncated icosahedron having 12 five-membered and 20 six-membered rings on the surface of a sphere has been proposed. The structure, which has been called buckminsterfullerene or footballene, has so far not been substantiated, but has attracted the attention of theoretical chemists as an example of a compound with possible spherical aromaticity.[187,188] According to the value of the resonance energy per π-electron this structure can be classed as aromatic, but judging by the ratio of the resonance energy to the total π-electron energy of the reference structure (% RE), the stabilisation energy is insufficient to isolate buckminsterfullerene in macroscopic quantities.[187] A theoretical analysis of the magnetic properties led to the conclusion that this compound should be very slightly diamagnetic.[189]

Thus, the types of stabilisation of molecules or ions that are described by forms of aromaticity constitute in the majority of cases unproven or rejected ideas. In the individual cases where the stabilisation effect has been established, it can be interpreted without difficulty independently of the concept of aromaticity. A wider interpretation of the concept of aromaticity is not appropriate since, not having a proper basis or being created through necessity, it has a destructive effect on the concept of aromaticity as a whole. The acceptance of a wider interpretation would signify a rejection of the elaborated experimental criteria of aromaticity, both magnetic, related to the ring current, and structural, which are inapplicable to non-planar or acyclic structures, and also ideas about the common nature of aromatic reactivity.

3. Extension of the concept of aromaticity. σ-Aromaticity.

The generally accepted ideas about the electronic structure of organic compounds are based on models, according to which π-electrons are distinct from the electrons of σ-bonds. It is assumed in this case that the σ-system consists of effectively localised two-centre, two-electron bonds, and that all deviations from additivity, including those related to aromaticity, are due to delocalisation of the π-system. However, both types of bond, both π and σ, can exhibit "localisation" and "delocalisation" to comparable degrees.[190] Additivity of the properties of σ-bonds is not due to the absence of σ-delocalisation but occurs because the interaction between neighbouring σ-bonds is approximately constant, does not depend on the environment, and in calculations is included in the empirical bond constants. As the individual sp^3-hybridised orbitals of a carbon atom interact effectively with each other, each CH_2 group in an alkane can be regarded as an equivalent valence group in a polyene. The system of hybrid orbitals of the C–C bonds in cyclopropane is topologically similar to the π-orbital system of benzene, while the cyclobutane system is topologically similar to the system of planar cyclooctatetraene. Therefore, by analogy with π-aromaticity and π-antiaromaticity, the question of the σ-aromaticity of cyclopropane and the σ-antiaromaticity of cyclobutane can be raised.[179,190] The concept of σ-aromaticity for cyclopropane can be used to explain its outstanding stability and other properties.[190,191] The same criteria of aromaticity as those for π-aromatic systems are applied to cyclopropane, including the cyclic delocalisation of electrons found in the magnetic properties from NMR spectroscopic data and the Dewar resonance energy, which constitutes 0.694 eV.[192] From an analysis of orbital interactions, electronic calculation rules for the determination of σ-aromaticity in cyclic structures have been formulated.[193,194] With an increase in size of the ring the degree of aromaticity decreases so rapidly that even in cyclopentane it is extremely small and cannot have any appreciable effect on its properties. Only π,σ-aromatic compounds, from which the greatest contribution is provided by σ-aromaticity in the cyclopropenium cation ($2\pi 6\sigma$), have a high stabilisation energy. In an article by Cremer[192] entitled "For and against σ-aromaticity", it is observed that the characteristics of cyclopropane may adequately be represented using the concept of "surface" overlap of the σ-orbitals instead of σ-aromaticity, while the characteristics of a tetrahedron[195] can be represented by "three-dimensional" overlap instead of three-dimensional σ-aromaticity.

It was important to determine how the inclusion of electrons from σ-bonds would effect the basic conclusions of the aromaticity concept that were derived from a model that took only π-electron delocalisation into consideration. It was shown by non-empirical calculations of the benzene molecule[196] that on going from a structure with D_{6h} symmetry to a Kekulé structure with D_{3h} symmetry and alternating bonds the π-electron energy decreases but the σ-electron energy increases to a greater degree, in other words, equalising the bonds is determined by the σ-skeleton. The question arises as to the legitimacy of using the equalising the bonds as a structural criterion of aromaticity related to the cyclic delocalisation of π-electrons. Calculation of the topological resonance energy (see Section III)[197] led to the separation of a component resulting from the cyclic π-electron delocalisation and having, as it transpired, the opposite sign to the change in total π-electron energy of the system. The decrease in the latter on distorting the symmetrical structure of benzene to a Kekulé structure occurs at the same time as an increase in energy of the cyclic π-electron delocalisation, as a result of which it is possible to balance the increase in σ-electron energy. On the other hand, in the case of the antiaromatic cyclobutadiene the change from a square structure to the structure of a rectangle with alternating bonds causes a decrease in both the total π-electron energy and the energy of the cyclic π-electron delocalisation, as a result of which the decrease in π-electron energy is not balanced by the increase in σ-electron energy and the structure with alternating bonds proves to be more stable. Thus, equivalence of bond lengths is in fact related to cyclic delocalisation of the π-electrons and can be

justified as a criterion of aromaticity. The concept of σ-aromaticity does not contradict the concept of π-aromaticity but complements it, as ideas about σ-conjugation complement the generally accepted theory of the structure of organic compounds.

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The current concept of aromaticity which is based on the progress in the synthesis of aromatic systems and their study using experimental physical techniques and theoretical quantum-chemical methods relates to conjugated cyclic systems that have cyclic delocalisation of electrons. As a special property of the electron shell, aromaticity is exhibited in their properties, from which magnetic, structural, and energy characteristics can serve as criteria of aromaticity, but reactivity cannot since it depends not only on the ground state but also on the transition state. The extension of the concept of aromaticity to systems that are devoid of cyclic declocalisation of electrons, resulting in ideas about multiple types of aromaticity, is unjustified and inappropriate. The common nature of the electronic structure and properties is responsible for the chemistry of aromatic compounds being formed as a separate branch of organic chemistry.

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Present ideas on the influence of the medium on acid–base equilibria. Hydrogen bonds in the gas phase and in solution

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ABSTRACT. Data on acid–base equilibria in different media and in the gas phase have been analysed. Methods for determining the protonation centre in a gas have been discussed. The change in the electronic effects of substituents on going from the gas phase to solution have been examined. The relationships between the strength of ionic hydrogen bonds and the acid–base properties of compounds in the gas phase have been demonstrated, and the results obtained by modelling solvation effects in the gas phase have been examined. New data on the structure and stability of molecular H-complexes in the gas phase and on the increase in the strength of the H-bond on solvation are presented.

The bibliography contains 130 references.

Contents

I. Introduction 134
II. The influence of hydrogen bonds with solvents on acid–base equilibria 134
III. Ionic hydrogen bonds in the gas phase. Relationships between the strength of these bonds and the proton affinity of the partners. Modelling solvation effects 139
IV. The structure of molecular H-complexes in the gas phase 141
V. Solvation of the H-bond 146
VI. Summary 148

I. Introduction

The development of new methods for studying proton transfer reactions in the gas phase (ion cyclotron resonance and high-pressure mass spectrometry) has led to a new attitude to the problem of the influence of the medium on the structure and reactivity of compounds. It has become clear that in the past the part played by these factors has been greatly underestimated. Solvation effects may be comparable with the electronic influence of substituents, and sometimes significantly greater.[1,2] In many cases, the part played by hydrogen bonds is decisive.[3,4]

In recent years, important data have been obtained on the energy of formation of ionic dimers and ionic clusters involving several solvent molecules in the gas phase. The energy of formation of a large number of these clusters has been compared with the energy of solvation of the ions by the solvent. In addition, analogies have been revealed in the solvation of ion–molecule and neutral H-complexes. New methods of high-resolution spectroscopy, which make it possible to establish the structure of intermolecular hydrogen bonds in the gas phase, are being actively developed. This information is direct and reliable, in contrast to that obtained by calculation or by analysing mass-spectrometric data.

Present ideas about the role of the medium in acid–base equilibria are based on a combination of experimental studies in the gas phase and in solvents of different types with quantum-chemical calculations, including in recent years calculations by the methods of molecular dynamics and Monte Carlo methods. The present review does not claim to cover completely all topics and all the published literature, but should provide reference points in this varied and rapidly developing field. Various methodological approaches which help to distinguish the role of hydrogen bonds in the influence of the medium on acid–base equilibria are analysed.

II. The influence of hydrogen bonds with solvents on acid–base equilibria

1. Acid–base properties in water and dipolar aprotic solvents

The basic concepts of the electronic effects of substituents were formulated from the study of acid–base equilibria in aqueous media. Historically, the first acids studied in this connection were benzoic acids and phenols, which ionise in water in an acidity range convenient for study. The subsequent study of acid–base equilibria in dipolar aprotic solvents (DAS) showed that the acidity scale is extended in these solvents, making it possible to distinguish the acidity of compounds having identical pK_a value in water. This characteristic of DAS is referred to as their "differentiating action".[5,6] The pK_a values in DAS and in proton-containing solvents (PS) for organic compounds of the same class are related by linear expressions of the type

$$pK_a(S) = \alpha pK_a + \beta, \quad (1)$$

where the coefficient α characterises the sensitivity to the influence of substituents in DAS. The value of α increases in the order H_2O < ROH < DAS. Deviations from the linear relationship are observed for acids with *ortho*-substituents, which form intramolecular hydrogen bonds or create appreciable steric hindrance.

The differentiating action of DAS increases with increase in the basic strength of the solvent.[7] Thus for benzoic acids the coefficient α increases in the solvent order: H_2O (1) < CH_3OH (1.3) < $(CH_3)_2CO$ (1.72) < CH_3NO_2 (1.81) < DMF (1.98) < CH_3CN (2.5) < DMSO (2.8).[8]

In an analysis of the differences between the pK_a values in N-methylpyrrolidone (NMP) and DMSO, Bordwell and co-workers[7]

examined various acids forming oxo-anions on ionisation (naphthols, phenols, benzoic acids, salicylic acid, etc.). The values of ΔpK_a = pK_a(NMP) – pK_a(DMSO) increase with decrease in the acidity from pK_a = 0.45 to pK_a = 1.95. In more basic anions, the charge localised on the oxygen atom is greater, and the difference in the stabilisation achieved in NMP and in DMSO increases. This is also indicated by data obtained in DMF and DMAA.[9] The pK_a values in NMP and DMSO are related by the linear expression:

$$pK_a(\text{NMP}) = 0.91 pK_a(\text{DMSO}) + b.$$

In the opinion of the authors cited, the acidity values in DMSO (of which more than 600 are known) can be used to predict the pK_a values in any carboxamide solvent, and in other DAS in the absence of strong ion pairing.

In the study of acid–base equilibria in DAS it is necessary to take account of the complicating action of "homoconjugated" hydrogen bonds between the acid and the anion.[3,9] The formation constants of these bonds in NMP[7] and in DMF[9] are ten times those in DMSO. The formation of homoconjugated ions is energetically favourable even in DMSO, however. Thus the equilibrium PhOH...DMSO + PhO^- ⇄ PhO^-...HOPh + DMSO is displaced to the right. The "homoconjugated" hydrogen bond PhO^-...HOPh is 6.1 kcal mol^{-1} more stable than the H-bond between phenol and DMSO.[10]

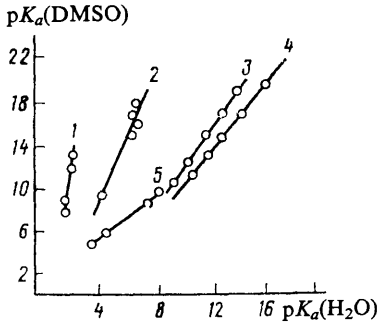


Figure 1. Relationship between pK_a (DMSO) and $pK_a(H_2O)$ for organic acids of different classes: *1*, benzoic acids; *2*, phenols; 3, nitroanilines; *4*, CH-acids; *5*, ammonium acids.[11]

The values of α in Eqn. (1) for XH-acids of different types in DMSO have been compared.[11,12] Fig. 1 shows that the value of α is greatest for benzoic acids, and decreases in the order:

$$XC_6H_4COOH\,(2.43) > XC_6H_4OH\,(2.14) > XCOOH\,(1.94) > X_2NH\,(1.55) > X_3CH\,(1.46) > X_3NH^+\,(1.14).$$

Acids in whose conjugate bases the charge is delocalised have a lesser ability to form H-bonds X^-...HOH with water as proton donor. Decrease in the stability of the H-complex with the anion is accompanied by a decrease in the difference between the acidities in water and in DMSO (OH > NH > CH > NH^+).

For charged (NH^+)-acids, substituents have practically the same influence in DMSO and in water (α = 1.1), since both solvents are good proton acceptors (NH^+...S).[11]

Another widely used method for estimating the sensitivity to the solvent of the effects of substituents is by comparing the coefficients ρ in the Hammett equation:

$$pK_a = pK_0 + \rho\sigma, \qquad (2)$$

where pK_0 is the value of pK_a in water, and σ a substituent constant. The value of ρ increases considerably on going from H_2O to DAS. This is demonstrated for benzoic acids and phenols in Table 1.

The difference in the values of ρ in the solvents CH_3OH and DMF, which belong to different groups (PS and DAS) but which have similar dielectric constants (ε), indicates that non-specific universal interactions have little influence. For benzoic acids, for example, the value of ρ in DMF is approximately 1.5 times that in CH_3OH (Table 1).

Table 1. Values of ρ in Eqn. (2) for phenols and benzoic acids in different media.

Compounds	H_2O	CH_3OH	C_2H_5OH	C_3H_7OH	DMF	CH_3CN	DMSO	Refs.
Benzoic acids	1.0	1.38	1.66	—	2.03	2.37	2.57	[8]
					2.3	2.4	2.4	[9, 10]
Phenols	2.1	—	—	2.25	4.5	4.7	4.88	[11]
							4.29	[9]
							5.3	[10]

To lower the influence of solvation factors, it is necessary to use the most inert solvents. The study of proton transfer reactions in these media is associated with a number of difficulties, including the low solubility of salts in these solvents, the formation of hydrogen bonds between the reagents, dimerisation of the acids, etc. The main complication, however, is that in media with a low polarity and low dielectric constants (ε = 2–6), ion pairs are not dissociated ($K_d \leqslant 10^{-8}$), so that the observed relative strengths of acids depend on the nature of the base chosen for comparison.[13]

The influence of the acidic and basic properties of the partners and the medium on proton transfer and the formation of ion pairs by an acid with a neutral base has been studied intensively in recent years by molecular spectroscopy and low-temperature NMR spectroscopy. This work has been reviewed in detail.[14,15] The extensive studies of the formation of strong hydrogen bonds and ion pairs with charged acids have also been reviewed.[16] †

2. Acid–base equilibria in relatively inert media

Acid–base equilibria in dimethoxyethane (DME), cyclohexylamine (CHA), and tetrahydrofuran (THF) have been studied for CH-acids which form highly delocalised carbanions and which do not tend to undergo ionic aggregation, and also for acids whose carbanions contain substituents with charges localised on them.[17,18] Data have recently been obtained on the acidity of polyarylmethanes and fluorenes in tetrahydrofuran,[19,20] and the pK values of sulphur-containing compounds in CHA and DMSO have been compared.[21]

† See also I S Perelygin *Ionnaya Sol'vatatsiya* (Ion Solvation), Izd. Nauka, Moscow, 1987, p. 164

Expressions relating the ion-air acidity in comparatively inert media with the "ionic" acidity in DMSO, in which the salts are completely dissociated, have been proposed.[22-24] Two types of equilibria were compared:

$$R_iH + R_0^- \ldots M^+ \rightleftarrows R_i^- \ldots M^+ + R_0H, \quad \text{in ethers and cyclohexylamine} \qquad (3)$$

$$R_iH + R_0^- \rightleftarrows R_i + R_0H. \quad \text{in DMSO} \qquad (4)$$

The ion-pair (pK_{ip}) and free-ion (pK_i) acidities are found from the usual relationship

$$pK = pK_0 + \lg K_d$$

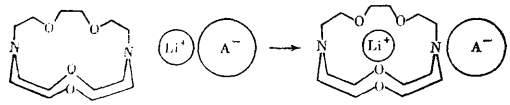
applied to equilibria (3) and (4). If the dissociation constants (K_d) of the ion pairs, which can be determined spectrophotometrically or conductometrically, are known, the pK_{ip} values can be used to obtain the free-ion acidity in media with a low polarity (pK'):

$$pK' = pK_{ip} + \lg(K_{d_0}/K_d), \qquad (5)$$

where K_{d_0} is the dissociation constant of the ion pair formed by a standard carbanion with the cation. The pK' values practically coincide with the pK_i values in DMSO. The differences between pK_{ip} and $pK_i \simeq pK'$ depend on the structure of the carbanion, and also on the ability of the cation to form ion pairs. They are greatest for anions in which the charge is localised on a substituent. The differences are greatest for the Li^+ cation, and decrease with increase in the cation size.

Data published in 1988 on ion-pair and ionic acidities in THF [20] show excellent agreement with these conclusions.[23,24] The difference in the values of the ion-pair and ionic acidities in DME and THF is less than 0.2 pK unit. The values of pK_a in THF, CHA, and DME are related by linear expressions, and the coefficient α is close to 1 (0.999–1.02).[21]

In a new approach to the study of acid–base properties in media with a low polarity and the analysis of the influence of solvation,[25,26] the use of the cryptates of organolithium compounds has been proposed for the construction of an acidity scale. The systematic spectral and conductometric study of the lithium salts of aliphatic and aliphatic–aromatic hydrocarbons in the presence of cryptands has established reliably that, irrespective of the polarity of the medium, they form ion pairs separated by the cryptand.



Thus 4,7,13,18-tetraoxa-1,10-diazabicyclo[8,5,5]eicosane forms a stable inclusion complex with the lithium cation, shielding it from the solvent and the anion. As a result, the ion-pair acidity in media with a low polarity is linearly related to the ionic acidity in DMSO with a coefficient α practically equal to 1. Thus for THF:

$$pK_a(\text{DMSO}) = 1.01pK_a(\text{THF}) + 17.2. \qquad (6)$$

The ionic acidity in the solvent in the absence of specific solvation was related to the acidity in the gas phase

$$\delta\Delta G^S(HA/HA_0)_i = \delta\Delta G_A^{gas}(HA/HA_0)_i + b/\varepsilon_S. \qquad (7)$$

Thus the ionic acidity under these conditions is a linear function of the quantity $1/\varepsilon$. The values of ΔG_A^{gas} obtained using Eqn. (7) coincided with the results of direct determinations (only four such determinations have as yet been carried out, however).

Thus it has now been reliably established that dipolar aprotic solvents have a differentiating action, which is due chiefly to the decrease in the strength of the solvation of the anions as a result of the formation of H-bonds. Approaches to the establishment of acidity scales for CH-acids in media with a low polarity have been found. The use of cryptands should make it possible to study the acid–base properties of acids of other types in these media.

3. Acid–base properties in the gas phase and in solution

Studies of acid–base equilibria, which are being carried out on an increasing scale, have accumulated a large amount of data on organic compounds of different classes (see the published reviews[2,3,27] and monographs[18,28]). These results have made it necessary to re-examine existing ideas about the electronic effects of substituents. The present theory of intramolecular interactions between a substituent and a reaction centre is based on non-empirical molecular orbital calculations, and the fairly approximate model of point charges is used for a qualitative examination (see the papers by Taft[2] and Koppel' [29] and references therein).

For most classes of organic compound, the sensitivity to the influence of substituents in the gas phase is greater than that in DAS, and much greater than that in water; in other words, using the terminology adopted to describe acid–base equilibria in solutions, the gas phase has the greatest "differentiating action". Since however the acidity in the gas is a characteristic "internal" acidity, it is more correct to speak of the action of the medium levelling the electronic influence of the substituents.

The chief factor for the levelling of the acidic properties in PS and in water is the formation of hydrogen bonds with the anions. Thus the sensitivity of benzoic acid derivatives to the influence of substituents is greatest in the gas phase; it is 1.6 times smaller in water, and almost 4 times smaller in DMSO.[2] An interesting feature is that the levelling action of an aqueous medium decreases with decrease in the ability of the anions formed to act as electron donors in H-complexes A^-...HOH, and is not observed for carbanions with a highly delocalised charge.[2,18] The order of change in the coefficient α in the series XC_6H_4COOH (10.6) > XC_6H_5OH (6.6) > XCOOH (3.5) > X_3CH (1) agrees with the order obtained for XH-acids of the same types in DMSO(see above).

Comparison of the heats of hydration and the thermodynamic characteristics of deprotonation in the gas phase and in water has shown that most of the gain in ionisation energy observed with increase in the electron-acceptor properties of the substituents is compensated by the decrease in the energy of hydration of the anion formed. The marked decrease in the ability of these anions to form hydrogen bonds is due to the delocalisation of the negative charge, and leads to destabilisation of the anions. The equilibrium is displaced towards the undissociated acid. As a result, the range of change in the acidity in water becomes narrower.[2,3] A generalised scheme for the influence of the solvent has been proposed;[30] it examines the specific interaction of the solvent with the acid and the conjugate anion, including the formation of H-complexes with substituents such as COR, NO_2, SO_2Ph, etc. For example, for *p*- and *m*-substituted phenols a rigorously linear relationship is observed between ΔG(gas) and $\Delta G(H_2O)$ (the coefficient α = 6.6), deviations from which are related to the specific solvation of the substituents.[30]

A detailed analysis of the influence of different solvation effects on the protonation of substituted pyridines[31-33] has established that the principal role in the decrease in the strength of the effect of

substituents in water is played by hydrogen bonds with the pyridinium ions (XPy...HOH). The energy of formation of ionic H-complexes is five times the energy of the neutral H-bonds of substituted pyridines $XPyH^+...O_2H$. The decrease in the range of change in the basic strength in water is determined by the opposed influences of the substituent on the formation of ionic H-bonds and on protonation. The solvation model of the hydrogen bond has provided a quantitative description of the levelling in water (a three-fold decrease in the strength of the effect of substituents) which shows good agreement with experiment.[31] The anomalously low basic strength of 2,6-di-t-butylpyridine in water is attributed to steric hindrance to hydration. This compound is a very strong base in the gas phase.[32] A similar effect was recently detected in the study of other sterically hindered pyridines.[33]

A comparison of the changes in the basic strengths of two groups of secondary amines in the gas phase and in water[34] showed that alkyl substituents have a marked levelling influence in H_2O ($\alpha = 4.3$). The introduction into the alkyl substituent of functional groups which contain heteroatoms and which delocalise the charge decreases this effect by a factor of 1.6 (Fig. 2). In aqueous medium there is not only a decrease in the electronic influence of the substituents but also a change in the relative contribution of the components of this influence. The effect of polarisability in the gas phase is predominant, but in water its role decreases sharply, compared with the inductive field effect. The same change in the contributions of the components of the electronic effect was also noted for other classes of organic compound.[2,29] For primary amines, the influence of solvation as a result of the formation of additional H-bonds is greater than the electronic influence of the substituent[34] (the point for R = H does not lie on the straight line in Fig. 2). The influence of hydrogen bonds on the ionic hydration of primary amines was previously examined[35] using data on monitored solvation in the gas (this approach is examined in more detail in the next section). The role of H-bonds has been confirmed by a theoretical analysis at the level of non-empirical quantum-chemical calculations.[36]

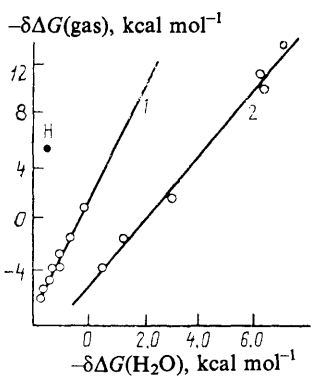


Figure 2. Relationship between the values of the basic strength $\delta\Delta G$ of secondary amines in the gas phase and in water: *1*, RNH_2 (slope 4.3); *2*, XCH_2NH_2 (slope 2.7).[34]

The study of acid–base equilibria in the gas phase has shown that solvation interactions can not only decrease the differences in the strengths of acids and bases but can also change the sequential order of compounds with similar structures.

A number of examples of opposite sequences of the change in the thermodynamic characteristics of the dissociation of substituted halogenoacetic acids, aliphatic alcohols, thiols, and amines in the gas phase and in water have been discussed.[1,2] The order of change in the acidity of aliphatic XH-acids in the gas phase is the opposite of that previously established for aqueous and aqueous-alcoholic media: in the gas phase, MeXH < EtXH < PrXH < t-BuXH, and in water t-BuXH < PrXH < EtXH < MeXH. Thus the strengths of these acids in water and alcohols are determined not by the electronic influence of the substituents but by solvation interactions with the corresponding anions.[2,37] According to quantum-chemical calculations, polarised alkyl groups may show either donor or acceptor properties, depending on the magnitude and sign of the charge on the X atom. A scale of polarisability parameters based on non-empirical calculations was recently published.[38]

The order of the acidity of alcohols in DMSO is the same as that in water,[39] that is although it is usually assumed that DAS solvate ions weakly, the energy of deprotonation in DMSO is not determined by "internal" factors. The role of ion–dipole interaction with DMSO requires further study.

The opposite order of change in the basic strength in the gas phase relative to solution was observed for methyl- and phenylphosphines.[40] The "internal" basic strength of Ph_3P (the proton affinity PA) is greater than that of Me_3P. At the same time, the basic strength of alkylphosphines in water is greater than that of phenylphosphines by several powers of ten. The same applies to the basic strength relationships for the phosphines in nitromethane.[11] Thus contrary to the published opinion,[12] nitromethane cannot be regarded as a medium in which specific solvation interactions are weak.

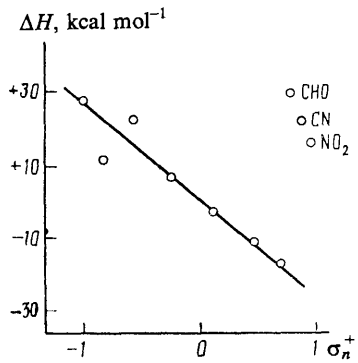


Figure 3. Correlation between the basic strength of PhX and the constants σ_n^+ of the substituents.[41]

The next step in the study of acid–base equilibria is the study of compounds in which transfer of the reaction centre is possible, and the identification of protonation centres in the gas phase.[41–47] For anilines, the coordination centre in solution is the lone pair of electrons of the nitrogen atom. The published conclusion[41] that the protonation of aniline in the gas phase involves the π-system of the ring was therefore surprising. The authors cited analysed the linear relationship between the basic strength of monosubstituted benzenes

in the gas phase and the σ^+ constants of the substituents. Fig. 3 shows that the points corresponding to compounds with strong electron-acceptor substituents do not lie on the straight line. The observed deviations towards higher basic strengths indicate that the ring is not the protonation centre in these cases. According to quantum-chemical calculations, protonation at nitrogen is energetically slightly more favourable than protonation at the ring,[42] but the differences are very small (1–3 kcal mol^{-1}). Finally, the basic strengths of fifteen substituted anilines in the gas phase have been compared[43] with the experimentally measured ionisation energies of the 1*s* electron of the nitrogen atom ($E_B N_{1s}$). A linear relationship between these quantities is observed for all the compounds except *m*-MeO-, *m*-MeS-, *m*-OH-, and *m*-NH_2-anilines, which are assumed to be protonated at the ring. Fig. 4 shows that the points corresponding to the "hydration" of these compounds in the gas phase, measured for the monitored addition of water ($BH^+ + OH_2 \rightleftarrows BH^+...OH_2$) also do not lie on a straight line. From this it was concluded that aniline in the gas phase is protonated at nitrogen, but that in various *meta*-substituted compounds with donor substituents the coordination centre is the benzene ring.

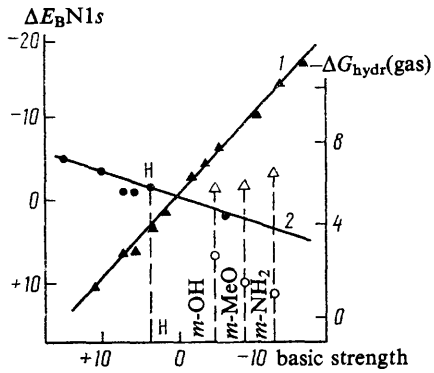


Figure 4. Dependence of the gas-phase basic strength of anilines on the ionisation energy of the N1*s* electrons (*1*) and on the energy of "hydration" in the gas phase ($BH^+ + OH_2 \rightleftarrows BH^+...OH_2$) (*2*).[43]

Single-parameter linear correlations between the PA values and the energies of the core electrons were previously observed for alcohols, ethers, carbonyl compounds, amines, and phosphines.[44] The existence of these correlations for compounds having two centres, for example amides (in which oxygen is the protonation centre), pyridines, and aminonaphthalenes,[45] made it possible to establish the protonation centres, and also to determine the conditions under which the correlation breaks down. In a number of studies, a similar analysis was based on empirical relationships between PA and the first ionisation potential (found by photoelectron spectroscopy). For example, a linear relationship was established between the proton affinity and the first ionisation potential of various compounds of phosphorus(III).[46] The points for cyclic and acyclic phosphites also lie on this straight line, indicating that the protonation centre in these compounds is the phosphorus atom, and not oxygen. The existing two-parameter expressions relating the PA to the energy of the electrons of the core and the first ionisation potentials[47] can be used to predict the protonation centre in the gas phase, since the correlation coefficients are different for O-, N-, and C-bases.

A successful solution to the problem of the protonation centre in the gas phase was recently achieved by comparing experimental data with the results of non-empirical quantum-chemical calculations.[48,49] A study of the protonation of phosphine oxide and the amides of acids of phosphorus(V) established that protonation takes place preferentially at the oxygen atom; the difference between the protonation energies of the oxygen and nitrogen atoms, according to quantum-chemical calculations, was 100 kcal mol^{-1}.[48] The basic strength of nitrogen-containing heterocyclic compounds in the gas phase has been examined.[49] A comparison of the PA values, the energies of the N_{1s} electrons, and the results of non-empirical calculations established that the protonation centre in a series of azaindoles is the nitrogen atom of the pyridine ring, and not the indole ring.

Without adding to the number of examples, mention may be made of various regular features of the change in the intramolecular interactions on going from the gas phase to solution. In this case it is possible to observe a levelling of the strengths of acids and bases, reversal of the sequence for compounds with similar structures, and a change in the protonation centre. The levelling action of the solvent indicates that solvation effects play a less important role than intramolecular effects. The reversal of the sequence indicates that the effect of the medium is stronger than the influence of the substituent.

In all cases, the influence of the solvent competes with that of the substituent. Among solvation effects, the most important role is played by the solvation of charged species (the anion A^- or the protonated base BH^+). The strength of the ion–dipole interactions and the energy of formation of hydrogen bonds are greater, the smaller the ion and the more localised the charge in it. Thus solvation effects bring about the greatest stabilisation of small ions. These ions, however, are less stable in the gas phase. Increase in the size of the anion and increase in the polarisability of the substituent increase the ability of the ions to delocalise their charge, leading to their stabilisation in the gas phase, and hence to an increase in the "internal" acid strength (basic strength). This effect is called "internal solvation".[1] At the same time, these ions are stabilised to a smaller extent under the influence of the solvation effects of solvents.

These ideas make it possible to understand the cases in which levelling of the eletronic effects should take place, and those ion which reversal of the sequences of the acid–base properties in solution or a change in the protonation centre should take place.

In those classes of organic compound including large molecules of similar size, such as aromatic and heterocyclic compounds (the benzoic acids, phenols, pyridines, etc. already examined), solvation effects decrease the difference in the acid–base properties. In *ortho*-substituted compounds with intramolecular hydrogen bonds or substituents with a large volume creating steric hindrance to solvation, however, the sequence of changes in the internal acid strength (basic strength) in solution may break down.[32,33] Deviations from the linear relationships between PA(gas) and $pK_a(H_2O)$ are also possible for substituents forming strong hydrogen bonds with water.[30]

Reversal of the order of change in the acid–base properties on going from the gas phase to solution can be expected in those

homologous series where the first members are compounds giving small ions and where the size and shape of the molecules change considerably with increase in the number of carbon atoms. This applies to aliphatic compounds such as alcohols, thiols, etc., and also to aliphatic compounds with substituents differing considerably in their polarisability and their ability to delocalise the charge on the ion. A change in the protonation position may take place if the potential protonation centres of the molecule have similar proton affinities and differ considerably in their ability to undergo solvation.[41,43]

The relative contributions of the components of the electronic effect change on going from the gas phase to solution (the polarisability effect is weakened to a greater extent than the inductive and resonance effects). The radical differences in the mechanisms of the stabilisation of ions in the gas phase and in solution require the special selection of materials for analysing intramolecular effects in compounds of different classes; it is necessary to compare compounds with similar dimensions and containing similar numbers of carbon atoms, that is compounds whose heats of solvation differ little.

III. Ionic hydrogen bonds in the gas phase. Relationships between the strength of these bonds and the proton affinity of the partners. Modelling solvation effects

Considerable progress in the understanding of the role of solvation has been made as a result of a range of studies of ionic hydrogen bonds in the gas phase. These studies are being carried out in two related directions: 1) the determination of the energy of formation of H-bonded cationic and anionic dimers, and the analysis of the relationships between the strength of the H-bond and the acid–base properties of the partners in the gas phase; and 2) the determination of the energy of H-bonds formed on the successive addition to the protonated ion of from one (in the dimer) to 4–6 solvent molecules, that is modelling the effects of solvation in the gas phase and comparing with solvation in solution.

1. Relationship between the strength of H-bonds in ionic dimers and the acid–base properties of the partners in the gas phase

On the basis of insufficiently accurate thermochemical data it was at first concluded that an overall linear relationship exists between the energy of the hydrogen bond AH...Cl^- and the acidity in the gas phase of acids of different classes.[50] It was later established[51,52] that this conclusion is erroneous. The examination of H-bonds of the type A^-...HOH and BH^+...OH_2 showed that these relationships are more complex. Fig. 5 shows the relationship between the energy of the H-bonds formed by different acids BH^+ with H_2O (NH_3) and the quantities $\Delta PA = PA(B) - PA(B_0)$, where $B_0 = H_2O$ and NH_3. For acids BH^+ of different types, a linear relationship between ΔH_{compl} and ΔPA is not observed. The slope of the curve increases from −0.12 for weak acids BH^+ (pyridinium ions) to −0.75 for the strongest acid (H_3O^+). An approximately linear relationship ws obtained for representative series of substituted pyridinium ions.

The energy of the strong hydrogen bonds AH...F^- and AH...Cl^- has been compared with the energy of proton transfer in the gas.[53,54] Linear relationships between these quantities were established for aliphatic alcohols. The points corresponding to acids of other types do not lie on the straight line. The magnitude of the deviations from linearity for the bonds XH...F^- depends on the electronegativity of the atoms. For similar gas-phase acidity, the energies of the H-bonds decrease in an order similar to that in solution: OH > NH > SH > CH.[53] The energy of the H-bond with Cl^- is less sensitive to the heteroatom joined to the acidic proton.[54] Similar conclusions were reached[55] in an analysis of the hydrogen bonds ROH...B^- with different anions. The stability of the H-complexes MeOH...^-RO in the gas phase depends linearly on the proton affinity of the anions OR^-. The hydrogen bonds formed by anions of other types (F^-, $C{\equiv}CR^-$, etc.) with similar proton affinities have different strengths, however. Table 2 shows that the enthalpies increase with increase in the electronegativity of the anion (χ). An expression relating the X^-...HY bond energy to the values of $\chi(X)$ and $\chi(Y)$ has been published.[56]

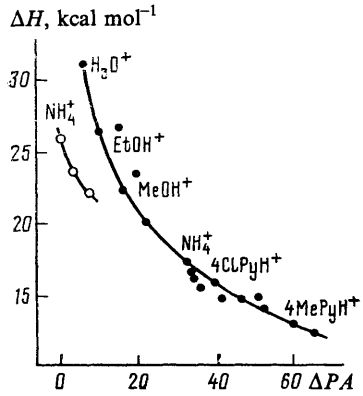
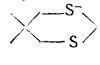


Figure 5. Relationship between the strength of the hydrogen bond BH^+...B and ΔPA (dark circles: $B_0 = H_2O$, light circles: $B_0 = NH_3$).[51]

Table 2. Stability of various bound dimers ($\Delta H_{0,1}$) and the group electronegativity of the anions (χ) in the complexes MeOH...B^-.[55]

B^-	$\Delta H_{0,1}$, kcal mol^{-1}	PA, kcal mol^{-1}	χ
F^-	29.6	371.5	4.0
$^-OCH_2$-t-Bu	18.6	371.8	3.5
$^-C{\equiv}CPh$	14.3	370.3	3.3
	14.8	372.9	2.5

The relationships between the stability of ionic dimers and the ΔPA values have been the subject of a large number of systematic studies.[57–60] Organic compounds of different classes, with a wide range of H-complex energies (ΔH_d^0) of 10–50 kcal mol^{-1} and ΔPA values 0–70 kcal mol^{-1}, were examined. The existence of the linear relationships

$$\Delta H_d^0 = \Delta H_d^0(0) - b\Delta PA, \qquad (8)$$

where $\Delta H_d^0(0)$ is the dissociation energy of the dimer with $\Delta PA = 0$, was reliably established.

Table 3 shows that these relationships are observed for many cationic complexes containing the heteroatoms of periods II and III (N, O, S). Anionic complexes have been less extensively studied; linear relationships between ΔH^0 and ΔPA were found for $O^-...HO$ systems.[60]

Table 3. Linear relationships between the energy of H-complexes ΔH_d^0 and the difference between the proton affinities of the partners ΔPA, Eqn. (8).

Type of complex	$-\Delta H_d^0(0)$, kcal mol^{-1}	b	n[a]	r[b]	Refs.
$NH^+...OH_2$	30.0	0.26	19	0.923	[57]
$NH^+...O$	28.3	0.23	48	0.979	[57]
$NH^+...N$	23.2	0.25	8	0.897	[57]
$OH^+...OH_2$	30.4	0.30	20	0.979	[57]
$SH^+...O$	18.6	0.164	6	—	[59]
$NH^+...S$	22.3	0.26	5	0.970	[57]
$NH^+...N\equiv C$	35.3	0.34	7	0.997	[58]
$H_3NH^+...N\equiv C$	32.7	0.38	4	0.984	[58]
$C\equiv NH^+...N\equiv C$	28.1	0.37	7	0.947	[58]
$OH^+...N\equiv C$	30.9	0.43	18	0.975	[58]
$C\equiv NH^+...O$	28.3	0.31	5	0.977	[58]
$RO^-...HO$	27.5	0.29	8	0.987	[60]
$RCOO^-...HO$	29.6	0.31	7	0.997	[60]
$O^-...HO$	28.1	0.29	13	0.981	[60]

[a] Number of systems studied. [b] Correlation coefficient.

An interesting feature is that the differences in the values of the slopes (b) of the linear relationships for complexes of different classes are small ($b = 0.2-0.3$). Increase in the polarity of the partners leads to an increase in the sensitivity of the energy of formation of the dimers to the ΔPA values. Thus for the H-complexes with nitriles, $b = 0.38$ for the $NH^+...N\equiv C$ system, and $b = 0.43$ for the $OH^+...N\equiv C$ system.[58] A low value of the coefficient b, 0.16, was also observed for the complexes $SH^+...O$.[59] For dimers of a different type, containing a less electronegative atom (sulphur) as the base ($NH^+...S$), however, the coefficient b has the usual value (0.26). In all the compounds studied, the highest dissociation energy is shown by the dimers whose partners have equal proton affinities ($\Delta PA = 0$). The inverse relationship between the stability of the H-complexes and the ΔPA values can readily be understood if the formation of the ionic H-bonds $HX^+...B$ is regarded as partial charge transfer.[56] Increase in the proton affinity of X makes the charged acid a less effective proton donor, and decrease in the value of PA for B leads to a decrease in the proton-acceptor properties. As a result, the energy of the H-complexes decreases with increase in ΔPA.

Analysis of the deviations from the linear relationship (8) helps to identify such structural features as the presence of intramolecular hydrogen bonds, the formation of multiple H-bonds in polyfunctional ions, and the existence of steric hindrance to solvation. Thus the bonds formed by polyethers, crown ethers, and polyamides with RNH_3^+ are stronger than might have been assumed from the dependence of ΔH_d^0 on ΔPA. The energy of the H-bonds increases by 8 ± 1 kcal mol^{-1} when a second bond is formed, and by 4 ± 1 kcal mol^{-1} when a third bond is formed. An interesting feature is that the enthalpy of formation of H-bonds for compounds with bulky substituents does not decrease if the optimum geometry of the H-complexes can be achieved in even one conformation. At the same time, steric hindrance leads to marked entropy effects, as shown by substituted pyridines with bulky substituents in the *ortho*-position.[33]

Various general trends in the change in the stability of H-complexes of the ionic type were recently analysed[61] for the case of hydride dimers. It was established that the strength of the H-bond in the symmetrical dimers generally increases from left to right along a period and upwards within a group, that is the order of change in stability with change in the position of the heteroatom in the periodic system shows a similarity between ionic and neutral dimers: (F, O > N > S > P) for $(AH_n)_2H^+$ and (F > O > Cl > Br > I > S > N > P) for $(AH_{n-1}^-...AH_n)$.

Comparison showed that cationic dimers are usually more stable than the corresponding anionic dimers. This was established for dimers containing oxygen, nitrogen, and sulphur atoms. The situation was different, however, for the most stable dimers, containing fluorine atoms. The enthalpy of formation of the $(FHF)^-$ ion is 39 ± 1 kcal mol^{-1}, which is greater than the corresponding value for $(HF)_2H^+$ and $(CH_3F)_2H^+$, 32 ± 2 kcal mol^{-1}.[61]

The authors cited consider that important characteristics of symmetrically bonded hydrides are the greater stability of the systems containing more electronegative atoms (F, O > N) and the absence of a correlation between ΔH and the basic strength. An interesting feature is that the strength of the H-bonds in symmetrical dimers, for example $OH^+...O$ and , remains unchanged when the hydrogen atoms of the hydrides are replaced by the most varied substituents. With wide variation in the substituents, the energy of formation $[-\Delta H_d^0(0)]$ of oxygen-containing symmetrical dimers is 31 ± 2 kcal mol^{-1}, and that of nitrogen-containing dimers is 23 ± 2 kcal mol^{-1}.[57] Like the coefficient b mentioned above, $\Delta H_d^0(0)$ increases with increase in the polarity of the partners. Thus the stability of the ionic H-complexes with nitriles is greater than that of the corresponding complexes with amines, although nitriles are weaker bases than amines.[58] Even smaller values of $\Delta H_d^0(0)$ are observed for complexes containing a sulphur atom (an element of period II).[59]

A non-empirical quantum-chemical calculation for cationic complexes[62] showed that for distances A–B shorter than 2.55 Å, a significant contribution to the energy is made by covalent bonding. This component increases with increase in the electronegativity of the atoms. The same conclusions were reached from non-empirical calculations at the highest level for unsymmetrical anion–water dimers.[63] On going from elements of the first period to the less electronegative elements of the second period (halogens, oxo- and thio-anions), the stability of the complexes decreases by 10–12 kcal mol^{-1}. Decrease in the covalent component is revealed by a decrease in the deviation from linearity of the optimum geometry of the complex. These deviations are less than 12° for localised ions of period I, and reach approximately 20° for ions of period II; for delocalised ions of period I (carboxylates, cyanides), the bending is intermediate. An examination of the relationships between the energy of ionic complexes and the ΔPA values,[62] and later studies,[64] confirmed the existence of linear relationships of type (8). The values of the slope obtained by calculation were close to the experimental values, and differed little for compounds of

different classes ($b \simeq 0.2$); a decrease in the energy of H-complexes containing elements of period II was predicted.

The same linear relationships of type (8) as for ionic H-complexes have been given for neutral hydrogen bonds.[65]

A general expression for the non-linear relationship between ΔH and ΔPA, covering ionic and molecular complexes, was proposed. The energy $\Delta H^0(0)$ for symmetrical dimers $(AH)_2$ obtained from these relationships, however, was 10–20 times the experimental value. The differences in the energies of dimerisation of $(AH)_2H^+$ (40–20 kcal mol^{-1}) and $(AH)_2$ ($\leqslant$4 kcal mol^{-1}) are so large that it appears impossible to find a general correlation equation applying to both ionic and neutral H-bonds.

2. Modelling solvation in the gas phase

High-pressure mass spectrometry has given useful results in the study of this problem.[57,66–68] Studies of ion–molecule equilibria of the type: $X^{\pm}(S)_{n-1} + (S) \rightleftarrows X^{\pm}(S)_n$ make it possible to determine the enthalpy ($\Delta H^0_{n-1,n}$) and free energy ($\Delta G^0_{n-1,n}$) of the addition of the nth molecule of the solvent (S) on the monitored addition of the latter ($n = 1-5$). Particular attention was paid to the study of hydration.

The total energy of the addition of n solvent molecules to the ions changes in the same order as the energy of formation of dimers by these ions. Thus the energy of formation of clusters (containing two and three water molecules) is greater for the 4-CNPyH$^+$ cation than for PyH$^+$, and the same is true of the energies of the dimers: 4-CNPyH$^+$...OH$_2$ > PyH$^+$...OH$_2$.[66] Similar trends were observed in the series $RNH_3^+...nH_2O$.[35] The total energy of formation of a cluster containing several water molecules approaches the energy of solvation by water as solvent. Analysis of the results of the study of varied onium ions,[57,66–68] supplemented by a comparison of the enthalpy of addition of four water molecules in the gas phase ($\Delta H^0_{0,4}$) with the values of the differences ($\delta\Delta H_{gas\rightarrow H_2O}$),[2] leads to a number of important generalisations.

It has been reliably established that the energy of the hydrogen bonds $\Delta H^0_{n-1,n}$ decreases with increase in n. This can readily be understood by taking account of the fact that the ionic charge is delocalised with increase in the size of the cluster. For singly protonated ions, the energy of addition of a second molecule ($-\Delta H_{1,2}$) is 0.7 $\pm$ 0.05 times the energy of the dimer ($-\Delta H_{0,1}$). The enthalpy of addition of a third molecule ($\Delta H^0_{2,3}$) is even smaller, and is equal to 0.85 $\pm$ 0.05 times ($-\Delta H_{1,2}$) As a result, the ratio of the total enthalpy of solvation of the ion with the addition of four H_2O molecules to the energy of the H-bond with one molecule ($\Delta H_{0,4}/\Delta H_{0,1}$) is constant for a wide range of onium ions; for singly protonated ions the value is 2.8.

A slight increase in this ratio ($\Delta H_{0,4}/\Delta H_{0,1} = 3.1$) is observed for ions of the type ROH_2^+, RNH_3^+, etc.

For most ions, the variation in the values of the enthalpies of solvation by water as solvent is determined completely by the variation in the strength of the hydrogen bonds. The energy of the specific hydration of BH$^+$ ions by four water molecules is close to the enthalpy of transfer $\Delta H^0_{gas\rightarrow H_2O}$ ($\pm$2 kcal mol^{-1}). Deviations have been observed only for ions containing phenyl substituents. The values of $\Delta H_{0,4}/\Delta H_{0,1}$ and the linear relationship (8) between the energy of the dimers ($\Delta H_{0,1}$) and the ΔPA values can be used to predict the energies of hydration of most onium ions. Modelling the effects of solvation for DAS gave similar results. The total energy of the addition of three DMSO molecules is 92% of the energy of solvation of the proton by this solvent.[69] The results of a non-empirical quantum-chemical analysis of this process have been published.[70] The energies of solvation was a result of the formation of H-bonds ($\Delta H_{n-1,n}$) by solvents of different types (ethers, ketones, amides, nitriles, etc.) have been compared.[57] In spite of the differences in the polarisability and dipole moments, in all cases the enthalpy decreases with increase in n, and the ratios $\Delta H^0_{0,n}/\Delta H^0_{0,1}$ are comparable with those given above for hydrated clusters. An interesting feature is that a similar relationship was found for hydrated metal ions (Li^+, Na^+, K^+).[71] Comparison of the "solvation" of a series of oxonium ions by acetonitrile in the gas phase with their hydration in the gas phase and in water[72] showed that the effect of hydration is similar to the effect of the formation of an H-bond with one CH_3CN molecule. According to the data obtained,[72] the relative free energy of solvation of the oxonium ions in water is twice the energy of formation of the hydrogen bond $OH^+...N{\equiv}CMe$ and three times the energy of the addition of one H_2O molecule in the gas phase.

A theoretical analysis of the addition of several solvent molecules, carried out successfully by model quantum-chemical calculations (STO-3G basis set), covers a large number (61) or oxo-anions.[29] The influence of mono-, di-, and tri-hydration on the geometry and extent of charge transfer was examined in relation to the size of the anion and the delocalisation of its charge. An example of the successful use of quantum-chemical calculations at this level for cations is provided by the calculation of the energy of solvation of primary amines in a cluster containing three water molecules.[36] Quantum-chemical calculations for ionic bonds have been reviewed in a recent book.‡

In recent years, considerable progress in the solution of problems related to the solvation of ions has been achieved by the methods of molecular dynamics (MMD) and Monte Carlo methods (MCM) using intermolecular potentials based on the results of non-empirical quantum-chemical calculations for the dimers. An example is provided by MCM calculations for carboxylate anions and ammonium cations,§ which gave important information on the structure of the solvation layers and the number and geometry of ionic hydrogen bonds.

Thus experimental studies of ion–molecule interactions in the gas phase, supplemented by determinations of the enthalpies of transfer of an ion from the gas phase to solution and quantum-chemical calculations, have demonstrated convincingly the relationship between the strength of the ionic hydrogen bonds in the dimers and the acid–base properties of the partners (in the gas phase). They have also established that the differences in the heats of solvation of ions in solution are determined by the formation of hydrogen bonds by the ions with several solvent molecules.

IV. The structure of molecular H-complexes in the gas phase

Mass spectrometry determines the energy examined above, but gives no information on the internal structure of free ionic H-complexes, for example the position of the proton in them. At the same time, the structure of many uncharged H-complexes in the

‡C A Deakyne *Structure and Energetics*, Vol. 4, VCH Publ. Inc., 1987, p. 105

§W L Jorgensen, J Gao *J. Phys. Chem.*, 1986, **90** 2174; G Alagona, P J Kollman *J. Am. Chem. Soc.*, 1986, **108** 185; see also the references given in these papers.

free state is now well known, but their energies have as yet been little studied. This complementarity of the data, on the one hand, sets the present section apart, but at the same time it may stimulate the theoretical generalisation of the two types of hydrogen bond.

In the last ten years, remarkable progress in the study of molecular H-complexes has been achieved by the use of high-resolution spectroscopy, primarily rotational microwave (MW) and vibrational (infrared) spectroscopy. Of key importance in this work has been the preparation of the specimen, involving deep adiabatic cooling (to ~ 10 K) of a supersonic gas stream or pulse expanding in a vacuum. The "freezing" of the thermal excitations in this molecular beam greatly simplifies the spectrum, which otherwise cannot be interpreted, and the elimination of particle collisions and the usual Doppler effect decreases considerably the lines due to the remaining transitions. The corresponding spectral apparatus makes it possible to resolve effectively the fine (rotational) and hyperfine (nuclear) structure of the spectrum, and its interpretation gives the detailed structure of the H-complex. Thus it is possible to determine the accurate equilibrium geometry of the complex, its deformation (zeroth amplitudes of the mutual orientation of the partners), the elasticity of the stretching and bending of the H-bond, and the increase in the length of the A–H bond on H-bond formation (to within $10^{-3}-10^{-4}$ Å). The fine structure of the infrared band can be used to determine the contraction of A–H...B on excitation of the proton vibration ν_S, and the displacements of the ν_S frequency can be measured with an accuracy which is 10^2-10^4 times greater than that when a broad band is used. After the "cold" rotational spectrum has been interpreted, it is possible to interpret the spectrum of the gas in thermal equilibrium, to determine low frequencies which cannot be measured directly, to estimate the elasticity and dissociation energy of the H-bond, etc. All these topics have been reviewed in detail.[73,74]

The number of complexes in a molecular beam is sufficient to make it possible to record the MW spectrum by sensitive MBERS (molecular beam electrical resonance spectroscopy) methods[73,74] and Flygare Fourier spectroscopy,[74] but is often insufficient to allow direct recording of the infrared spectra of the same complexes (the proportion of radiation absorbed is too small). It is possible, however, to detect changes in the actual beam (an increase or decrease in the number of particles in a given state) as a result of vibrational excitation or photo-dissociation of the complexes by the sufficiently powerful infrared radiation of a tunable laser. This method makes it possible to obtain good high-resolution infrared spectra (and also to estimate the lifetime of the excited complexes, opening up new possibilities for the study of the kinetics of the elementary acts); the results have been reviewed.¶ Thus the new spectroscopy has successfully brought "non-rigid" molecular complexes with their unavoidably large zero-point vibrations into the general sphere of the traditional spectroscopy of simple molecules.

In a few years, intensive spectral studies have examined a wide range of systems, mainly heterodimers of the type AH.B. A published list[74] gives 68 complexes of different AH from hydrogen fluoride to fluoroform and acetylene with various partners B from ammonia to nitrogen. In addition, the simplest triatomic complexes of AH with noble gases (9 systems) and cyclic heterodimers of carboxylic acids and amides (14 systems) have been studied.[73] A large amount of information leading to important conclusions has been accumulated, and is increasing rapidly (becoming broader, deeper, and more accurate), and includes associates with a high multiplicity, new dimers, the isomerism of H-complexes, their stability and dynamics, etc. (see the Summary).

The structures of a representative series of H-complexes from the simplest to the more traditional, established from the rotational spectra, are shown in Fig. 6, and Table 4 gives as an example the parameters of selected complexes from the most widely studied series FH.B. Some of the results and conclusions may be noted.

Table 4. Parameters of various H-complexes B...HF;[73,75] R = interatomic distances; μ_a and $\Delta\mu$ are the longitudinal component of the dipole moment and its increase in the complex; k_σ is the H-bond stretching force constant.

B	R_{FB}, Å[a]	R_{HB}, Å	μ_a, D	$\Delta\mu$, D	k_σ, N m^{-1}
Ar	3.5095	2.58	1.3353	—	1.4
N_2	3.082	2.16	—	—	5.5
CO	3.047	2.12	2.352	0.55[b]	8.5
CO_2	2.93	2.00	2.2465	0.60	2.2
NCCN	2.862	1.94	—	—	14.2
HCN	2.796	1.87	5.612	0.80	18.2
CH_3CN	2.759	1.83	—	—	20.1
$(CH_3)_3CCN$	2.725	1.80	—	—	—
NH_3		1.78[b]	—	1.3[b]	—
C_2H_2	3.075[c]	2.15	2.3681[b]	0.65[b]	—
C_2H_4	3.141[c]	2.21	2.384[b]	0.67[b]	—
C_3H_6[d]	3.021[c]	2.09	—	—	11.5
HF	2.79	1.86	2.9885	0.60	13.6
H_2S	3.25	2.32	2.6239	0.78	12.0
H_2O	2.69	1.80[b]	4.07	0.96	24.9
$(CH_2)_2O$	2.627	1.70	3.85	0.99	—
$(CH_2)_3O$	2.586	1.66	—	—	—

[a] A recent recalculation of some of the R_{FB} values with improved averaging with respect to the zero-point amplitudes gave differences of 0.005–0.017 Å (A C Legon, D J Millen *Chem. Phys. Lett.*, 1988, **147** 484); this probably provides a measure of the accuracy of the values; [b] data of Peterson and co-workers[76]; [c] from the C–C line; [d] cyclopropane.

Linearity of the H-bond. It has been established by direct experiment that an isolated single H-bond is in fact linear, that is the three atoms A–H...B lie on the same straight line;[73] previously, this was only postulated, on the basis of crystallographic data. The slight deviations from linearity obtained in non-empirical calculations for the simplest H-complexes[77] are comparable with the uncertainty in the measurements (5–10° [73]), and it is not clear how real these are.

Non-rigidity of the H-bond. It has been shown that the H-bond has a low rigidity and is easily deformed, particularly round the electron-donor atom B; this also agrees with crystallographic data. Thus in $CH_3C{\equiv}N...H-F$, the force constant of the bending of the H...N≡C angle is 3–4 times lower than that for the F–H...N angle[74] (and, like the chemical bonds in molecules, is 10 times lower than the force constant of the stretching of the H-bond). This "flexibility" of the H-bond corresponds to the high zeroth amplitudes of the angles of orientation of the partners. For example, the average values of the angles of rotation (libration) of HF in its complexes with H_2O, CO_2, and Ar are 18 3, 25.17, and

¶ R E Miller *Science*, 1988, **240** 447

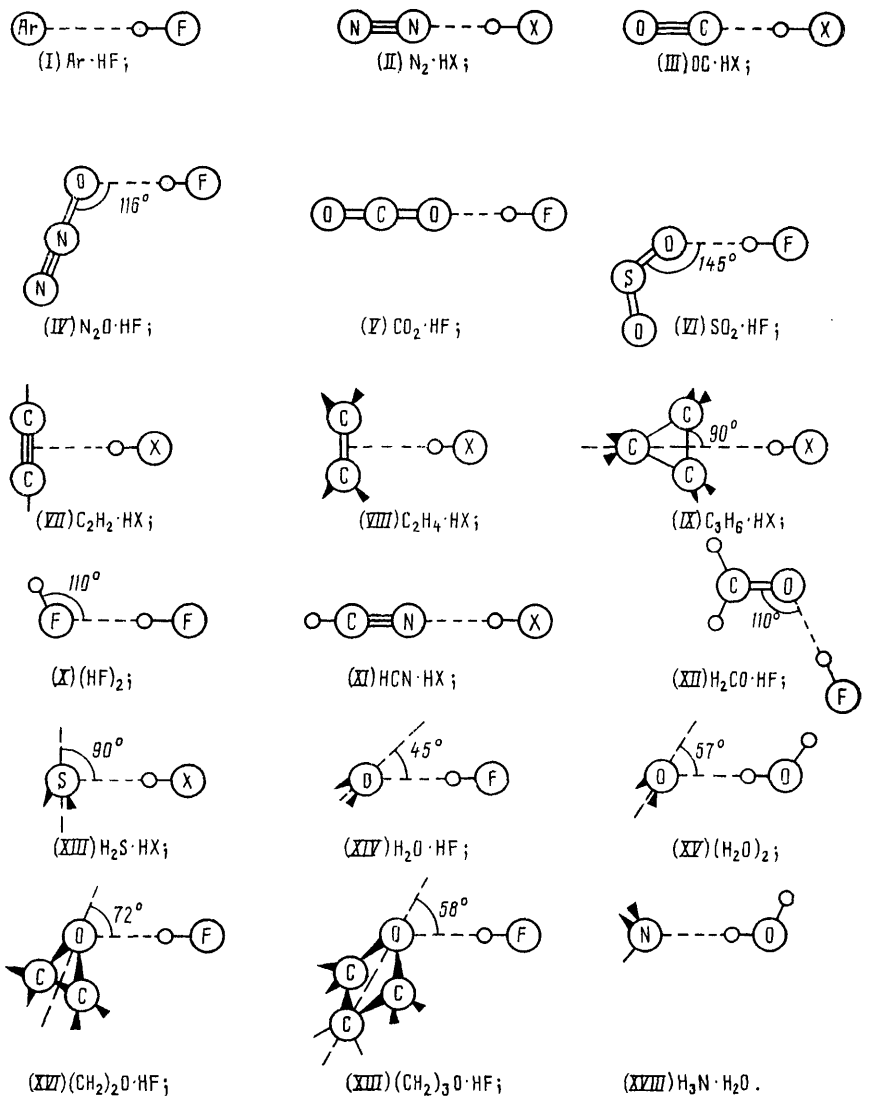


Figure 6. Configurations of various gaseous H-complexes AH.B, established from the rotational spectra;[73–75] for the interatomic distances A...B and other parameters see Table 4.

41.27° respectively.[73,76] At ordinary temperatures, when the librations are highly excited, the configuration of the H-complex should differ to an even greater extent from that shown in Figure 5 (the equilibrium configuration). It is the non-rigidity (difficulty of averaging) that limits the accuracy of the determination of the equilibrium geometric parameters of the H-complex from the extremely accurately measured rotational spectrum; the same applies to the dipole moments.

The flexibility of the complexes corresponds to the low wavenumbers of the librations of the sub-molecules (ν_β). They have not yet been observed directly in the spectrum, but are calculated indirectly from the changes in the spectra with change in temperature, or from the amplitudes of the angles. For the lightest hydrides, the values of ν_β reach 40–70 cm^{-1},[74,78–80] but in ordinary H-complexes they do not usually exceed 10–30 cm^{-1}. The excitation of these librations of the partner molecules is the main reason for the unique broadening of the vibrational bands by the H-bond at ordinary temperatures[78,79,81] (see, however, the papers by Millen[80] and Sokolov and Sakun[82]). The broadened band corresponds to a whole set of vibrational transitions, and not to one normal vibration. In this respect, the vibrational spectra of a complex AH.B and a simple molecule XYZ differ considerably. To make them comparable, it is necessary either to heat XYZ above 3000 K or to cool AH.B below 30 K, as is done in molecular beam spectroscopy.

Configuration of H-complexes. The orientation of the partners of the H-complex (in particular diatomic complexes; see the HF dimer in Fig. 6) is completely different from the favourable orientation of the dipoles. This is consistent with the known fact that there is no correlation between the dipole moment and the strength of the H-bond.[83]

The direction of the H-bond to some extent corresponds to the directions (valence angles) of the chemical bonds of the molecules (Fig. 6). Protonophiles of the first period tend to adopt the tetrahedral orientation, but hydrogen sulphide adopts the orthogonal orientation; a characteristic feature is the difference in the angles of the H-bonds with different cyclic ethers.[73]

In their systematisation of experimental data, Legon and Millen formulated the following rules. "The gas-phase geometry of a dimer B...HX can be obtained in terms of the non-bonding and π-bonding electron pairs on B as follows: (i) the axis of the HX molecule coincides with the supposed axis of a non-bonding pair as conventionally envisaged, or, if B has no non-bonding electron pairs but has π-bonding pairs, (ii) the axis of the HX molecule intersects the internuclear axis of the atoms forming the π-bond and is perpendicular to the plane of symmetry of the π-orbital. Rule (i) is definitive when B has both non-bonding and π-bonding pairs".[74]

These rules are not absolute. The pyramidal structure of $FH.OH_2$ [(XIV) in Fig. 6] has only been calculated for the equilibrium configuration, but in fact is not realised; the barrier to inversion is so low (0.36 kcal mol^{-1}) that the complex is effectively planar. Other complexes $XH.OH_2$ are even more likely to be planar, and the equilibrium pyramidal structure is only assumed.[74] Finally, the weak H-complex $HCCH.OH_2$ is recognised as definitely planar.[76] The hydrogen bond formed by AH with benzene is directed towards the centre of the ring at right angles to its plane,[74] and the (stronger!) bond with cyclopropane lies in the plane of the ring and is directed towards the centre of a C–C bond [(IX) in Fig. 6]. The dimer $CO_2.HF$, which is isoelectronic with $N_2O.HF$, is not bent like this compound, but is linear, contrary to the "rules" [(IV) and (V) in Fig. 6]. With weaker electrophiles, in particular HCN, the same CO_2 now forms a *T*-shaped complex $O_2C.NCH$ with an intermolecular C...N bond,[74] and not the isomeric linear complex OCO...HCN with an H-bond (energetically less favourable, but also observed later). A similar structure is shown by the symmetrical complex with water, $O_2C.OH_2$; this intermolecular C...O bond shows some similarity to a double bond (the internal rotation of H_2O is strongly hindered).[76] On the other hand, the "rules" are apparently applicable to stronger ("ordinary") H-bonds.

Structure of the dimers $(AH)_2$. The actual existence of the rotational absorption spectrum excludes non-dipole cyclic homodimers, and in fact all $(AH)_2$ studied are open and have a single H-bond AH...AH [(X) and (XV) in Fig. 6]. It has been shown, in particular, that the $(HF)_2$ ring is an unstable state corresponding to a saddle point of the potential.[76,77] The initial assumption that the dimer of methanol (and water) in a matrix is cyclic[83] was found to be due to the insufficient resolution of the infrared spectrum; improvement of the resolution showed clearly that the dimer is open[84] (as in the case of water also[85]). The free dimer of water [(XV) in Fig. 6] is now one of the most fully studied H-complexes.[73,74,76]

Thus prolonged argument has concluded that the dimers are open; four-membered $(AH)_2$ rings with the corresponding non-linear (90°) hydrogen bonds apparently do not exist. Other gaseous dimers, formed by CH_3OH, C_2H_5OH, H_2S, CH_3SH, CH_3NH_2, and $(CH_3)_2NH$, also have a dipole moment and therefore cannot be symmetrical rings, and are probably also open. The polymeric associates of these molecules, on the other hand, are non-polar and probably have a cyclic structure.[73]

Nature of the hydrogen bond. The data on the geometry of H-complexes have been interpreted from different viewpoints. In Dyke's opinion, the configuration of H-complexes indicates that "...the hydrogen bond is essentially covalent",[73] and the experimental results show excellent agreement with the HOMO/LUMO donor–acceptor model.[86] In the latter, the H-complex is regarded as an electron donor–acceptor complex, in which the electron pair is transferred from the highest occupied molecular orbital (HOMO) of the Lewis base to the lowest unoccupied molecular orbital (LUMO) of the Lewis acid, and the maximum overlap of the HOMO and LUMO is achieved in the dimer.[73]

In the opinion of Legon and Millen,[75] however, the orientation of the molecules is determined only by the favourable orientation of their dipole and quadrupole moments, and the experimental results are successfully described by a recent electrostatic model.[87]

It should be remembered, however, that simple electrostatics, that is the attraction of charges which remain unchanged in the interaction, cannot explain the distinctive spectroscopic and chemical properties of the hydrogen bond, namely the unique increase in the intensity and decrease in the frequency of the longitudinal vibration of the proton, the non-additivity of the dipole moments of the partners, and, finally, the cooperative effect—the significant increase in the strength of alternating H-bonds. Thus simple electrostatics apparently represents an unjustified resurrection of long abandoned ideas. Naturally, simple electrostatics cannot be identified with the so-called electrostatic (more accurately, Coulombic) contribution, distinguished in the non-empirical calculation of the energy of the H-bond. It hardly appears possible, however, to isolate the corresponding contribution from the experimental values to confirm the theory directly.

Interatomic distances. The lengths of H-bonds, which until recently were known only for crystals, have now been determined for various single H-bonds in isolated gaseous dimers, including the simplest and most important. In the complexes FH.NC the length of the hydrogen bond changes in accordance with the protophilic character of the nitrile group, but this regularity is not observed in the lengths of more varied H-bonds F–H...B (Table 4). The weak bond with CO_2 is shorter than the stronger H-bonds with π-electron donors and with cyclopropane; the H...B distances change less regularly than the classical spectral characteristics of the H-bond.

Comparison of the interatomic distances provides new and convincing confirmation of the cooperative character of H-bonds; the H-bonds of the polymer chains in HF and H_2O crystals are appreciably shorter than the bonds in the dimers; the difference is 0.30 Å and 0.14 Å respectively.[73] The O–O distances in the chain crystals of formic and acetic acids (2.58 Å and 2.61 Å respectively) are also appreciably shorter than those in the heterodimers of carboxylic acids (2.67 Å); according to Dyke,[73] this decrease in the length of the H-bond in the crystal may be due to the stronger cooperative effect in the chain of H-bonds, compared with the ring. Other factors may also be responsible, however: the higher temperature of the gas and the freedom of deformation of the dimer. A cooperative effect is also observed in gaseous trimers, that is when two H-bonds are conjugated. Thus the H-bonds in the linear trimers HCN.HCN.HA are 0.107–0.030 Å shorter than those in the dimers HCN.HA, where A = F, Cl, CN, CF_3.

The increase in the A–H distance on H-bond formation has been measured accurately in a number of dimers, and it has been shown that this increase in length rises approximately linearly with increase in the strength of the H-bond.[74] Direct confirmation has been

obtained for the long-predicted Stepanov–Sheppard effect,[88,89] that is the decrease in the length of A–H...B when the stretching vibration of the proton is excited; in HCN.HF it is 0.034 Å.[74] The existence of the opposite effect, that is a decrease in the strength of the H-bond as a result of the transverse vibration of the proton (ν_B), is indicated by the opposite "shading" of the rotational structure of the ν_B sub-bands.

Energy and elasticity of the H-bond. The values of $D_0(D_e)$ that is the energies of the dissociation of a free H-complex from its ground state (from the potential minimum), have been determined for the hydrogen bond for the first time (only a few have as yet been determined); the values, given in Table 5, were found from the measured "absolute" intensity of the lines in the spectrum of the equilibrium gas. This new and fundamental information (which will probably increase), combined with the highly accurate spectral parameters of the complexes, provides a fundamentally important supplement to ordinary thermodynamic and spectral data on H-bonds (plentiful for the condensed phase, but not for the gas phase).

Table 5. Dissociation energies of hydrogen bonds, from high-resolution spectra.

H-complex	Dissociation energy[a], kcal mol^{-1}		Spectrum	Refs.
	D_0	D_e		
HCN·HF	4.51 (26)	6.23 (38)	MB	[74]
»	4.96 (5)	6.87 (11)	i.r.	[90]
HCCCN·HF	4.87 (17)	5.59 (21)	MB	[91]
CH_3CN·HF	6.23 (14)	6.93 (21)	MB	[92]
HF·HF	2.97 (11)	4.56 (28)	i.r.	[93]
HCl·HCl	1.23 (6)	2.27 (25)	i.r.	[93]

[a] D_0 and D_e—measured from the lowest level and from the potential energy minimum.

The stretching force constant of the H-bond k_σ is determined accurately from the centrifugal stretching of the H-complex from the rotational spectrum.[74] A large number of "rotational" k_σ have now been obtained (an example is given in Table 4); these values are apparently more reliable than the previous isolated determinations of ("vibrational") k_σ from the frequency of the ν_σ bands, difficult to observe, in the far infrared region of the spectrum. Far infrared spectroscopy is also developing successfully (see for example the published review†), and a significant breakthrough is possible with the appearance of tunable lasers. Because of the difference in the selection rules, the two types of spectra should usefully supplement one another.

Comparison of the published[75] values of k_σ shows a mutual proportionality of the k_σ values in corresponding series of complexes AH.B (Fig. 7), similar to the proportionality of the enthalpies of the H-bonds.[94] As in the work cited,[94] it is possible to express this mutual independence of the proton-donor (P) and electron-donor (E) functions in the H-bond of any two partners, $(AH)_i$ and B_j, as the product $(k_\sigma)_{ij} = k_{11}P_iE_j$, where k_{11} is the normalisation to the standard H-complex with $P_1 = E_1 = 1$. A key question in this extension of the product rule[94] to k_σ is whether the two P and E scales (the scale constructed from ΔH in the liquid phase[94] and the new scale constructed from k_σ for the free H-complexes) coincide. For example, the electrophilic character of hydrogen fluoride (P = 1.9) estimated from k_σ (Fig. 7) is greater than that estimated from ΔH (P = 1.5 [94]) (this is only a preliminary estimate without conclusions). In general, the new data make it possible to compare on a more reliable basis two different measures of the strength of the H-bond, namely the dissociation energy and the quasi-elastic constant.

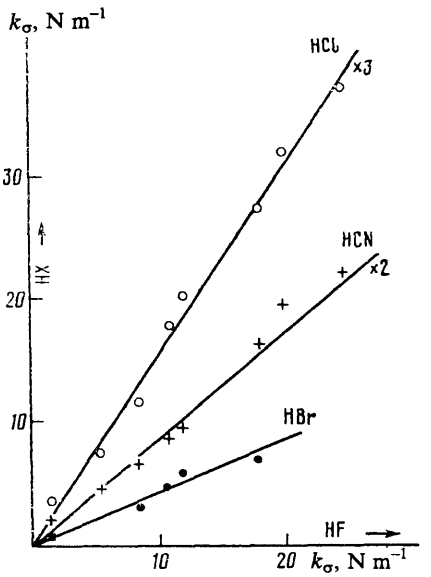


Figure 7. Relationship between the force constants of H-bonds of different proton donors HX with indentical protonophiles B in the gas phase, constructed from the data of Legon and Millen.[75]

Dipole moments. The extremely accurate dipole moment of a H-complex from measurements of the Stark effect in the microwave spectrum is the projection of μ on the prolate top axis; the total moment μ is established less accurately, because of the poor determination of the perpendicular components. For H_2S.HF, for example, the projection μ_a = 2.6239(17) D, and μ = 2.80(7) D.[73] To separate the induced moment $\Delta\mu$, it is necessary to subtract from μ_a the projections of the moments of the sub-molecules AH and B, not for the equilibrium configuration of the H-complex but with appropriate averaging with respect to the zeroth amplitudes. In spite of the difficulty of taking account of the non-rigidity of the H-complex in this way, the non-additivity of the dipole moments of the partners in the H-complex, that is the appearance of an additional excess moment $\Delta\mu$ (Table 4), has been reliably established.

†E Knozinger, O Schrems in J R Durig (Editor) *Vibrational Spectra and Structure*, Elsevier, 1987, Chapter, 3, p. 142

In some cases, the quantity $\Delta\mu$ can be attributed to the polarisation of one partner by the other, but in other cases this explanation is insufficient. For example, in $H_2S.HF$, $\Delta\mu$ is 0.2–0.6 D greater than that from the calculated polarisation and "...this contribution is very probably due to the charge transfer characteristic of the donor–acceptor model".[73]

In the particular case of the centrosymmetric protonophiles N_2 and NCCN, it is possible to estimate the redistribution of charge within the protonophile resulting from the H-bond. Movement of the two symmetrical N nuclei, identical in this case, is excluded, and the electrical asymmetry of the protonophile in the H-complex is revealed. The calculated N → N charge transfer is 0.025 e (see the paper by Legon and Millen[74] for more details). This means that not much can be expected from the traditional estimation of the values of $\Delta\mu$ for H-complexes in solutions from a simple vector scheme. The model of a "rigid" complex in this case is even less favourable, since at room temperature the deformations are much greater than in a cold molecular beam.

V. Solvation of the H-bond

The influence of a solvent on neutral H-bonds is qualitatively similar to its influence on ionic bonds, but is weaker than in the case of acid–base equilibria; in particular, it does not reverse the sequences of the strengths of acids and bases. This is partly due to the narrower range of liquids, not including associated liquids (water etc.). In addition, the magnitude of the influence differs considerably.[95] Non-polar $(AH)_n$ rings remain almost unchanged on going from the gas phase to solution; the liquid environment has no significant influence on the H-bond in this extreme case of the formation of a non-dipolar associate. At the same time, polar dimers AH.B undergo fairly marked changes in solution; the solvation effect may be greater than the primary effect of free H-bond formation. Finally, in the extreme case where the strength of the H-bond of the polar dimer AH.B is close to its limit, solution or condensation leads qualitative changes, bringing about the transformation of the molecular complex AH.B into the "conjugate" complex $A^-.H^+B$ or into the salt. The subsequent discussion deals mainly with the non-ionising solvation of the H-bond, and ionising solvation is mentioned only briefly.

Available data on the energy of H-bonds in the gas phase are insufficient for a reliable comparison with their energy in the more extensively studied liquid phase. A clearer picture of the influence of the medium on the H-bond is given by an analysis of the infrared spectra. Infrared spectroscopic data show that the solvation of a complex always leads to an increase in the strength of the H-bond.[94–96] According to these data, the transfer of a gaseous associate to the condensed phase: 1) lowers the frequency of the stretching vibrations ν_S (Table 6), 2) increases the frequency of the deformations ν_B, and 3) increases the absolute intensity of the vibrations ν_S. Each of these changes is a reliable spectral indication of an increase in the strength of the H-bond.[83,97] They all show quantitative consistency, that is they correspond to the same increase in the strength of the H-bond.[95] Thus dissolving free $FH.NCCH_3$ in acetonitrile lowers the ν_S frequency by 350 cm^{-1} (Table 6), and simultaneously displaces the ν_B band from 587 cm^{-1} to 750 cm^{-1}.[96] According to published correlations,[97] both displacements correspond to an increase in the energy of the H-bond from 5 kcal mol^{-1} to 8 kcal mol^{-1}. When gaseous $(CF_3)_2CHOH.NH_3$ is dissolved in dichloroethane, the intensity of ν_S increases by 10^5 cm $mmol^{-1}$;[95] this corresponds to an increase in the energy of the H-bond by ~4 kcal mol^{-1}, and is also consistent with the increase in $\Delta\nu$ from 500 cm^{-1} to 970 cm^{-1} (Table 6).

Table 6. Displacement $\Delta\nu = \nu_0^0 - \nu$ of the ν_S bands for various H-complexes in the gas phase and in liquids (solution in CCl_4 and in the liquid base B).[80,95,98–102]

Complex AH.B[a]	Δν, cm⁻¹			Complex AH.B[a]	Δν, cm⁻¹		
	gas	CCl_4	B		gas	CCl_4	B
CH_3OH.	(3682)[b]			$(CF_3)_3COH$.	(3630)		
Dimer	90	154	200[c]	Nitrile	275	390	480
Polymer	300	342	340	Water	280	372	—
Nitrile	58	107	141	Oxiran	355	440	—
Ether	123	184	175	m-Ether	440	565	—
Acetone	90	156	166	DMSO	610	820	1010
Pyridine	210	320	425	Pyridine	900	1150	1450
Ammonia	177	310	375[d]	Ammonia	750	—	—
TEA	370	460	438	CF_3COOH.	(3589)		
CF_3CH_2OH.	(3657)			Dimer	510	560	—
Nitrile	104	166	203	HF.	(3961)		
Oxiran	141	207	—	Dimer	80	—	—
Ether	220	268	267	Polymer	500	520	550
THF	220	289	312	Nitrile	300	485	650
Pyridine	370	530	580	m-Ether	500	—	740
Ammonia	310	540	—	Ether	575	740	750
$(CF_3)_2CHOH$.	(3646)			HCl.	(2886)		
Nitrile	148	250	326	Nitrile	155	275	335
Water	150	260	—	m-Ether	316	486	—
Oxiran	235	320	—				
Ammonia	500	760	970[d]				

[a] The names of the bases B are abbreviated: nitrile = acetonitrile; ether and m-ether = diethyl and dimethyl ethers; TEA = triethylamine; [b] the frequencies ν_0^0 of free AH in the gas phase are given in brackets; [c] in chloroform; [d] in dichloroethane.

The decrease in the ν_S wavenumber in solution has been most extensively studied; it was first observed by Allerhand and Schleyer[98] (although the authors cited did not attribute it to an increase in the strength of the H-bond), and was confirmed in subsequent experiments[95,96,99–109] and is shown in Table 6. The solvation effect depends not so much on the polarity of the medium as on the polarity of the associate and the dimensions of the partner molecules.[95] The solvation displacements $\Delta\nu_S = \nu_S(gas) - \nu_S(solution)$ in highly polar solvents (acetonitrile, DMSO) is only ~70% greater than $\delta\nu_S$ in the "inert" CCl_4, and in a given medium the displacements for polar complexes are ten times those for non-polar complexes (Table 6).

The medium has its weakest influence on non-dipolar cyclic associates, that is $(RCOOH)_2$, $(ROH)_4$, and $(HF)_6$.[95] The displacement of their ν_S band in solution is only 10–15% of the displacement $\Delta\nu^0$ in the gas, and the spectra of $(RCOOH)_2$ are similar to the gas-phase spectra not only in solution but also in crystals.[103–105] A surprising feature is that the ν_S bands of the gaseous cyclic formations $(CH_3OH)_4$ and $(HF)_6$ also undergo almost no displacement in liquid methanol and hydrogen fluoride (Table 6). In these associated liquids, the original rings undoubtedly are not preserved, and undergo rearrangement to give polymeric chains $(AH...)_n$, but the change in the long-range order of the H-bonds

does not influence the H-bond itself. This is consistent with the recently observed fact[107] that the infrared spectra of associated alcohols is independent of their concentration in solution (above ~1 M).

This absence of change in the spectra and hence in the H-bonds in $(AH...)_n$ is observed with a marked increase in the dielectric constant ε of the medium from 1 in the gas to 85 in liquid HF. Thus ε does not influence the H-bond, and correlations between its strength and ε are not significant. A similar lack of sensitivity to the environment is shown by the non-dipolar centrosymmetric ion $(FHF)^-$; in different media from water to the crystal, the frequency $\nu = 2500$ cm^{-1} changes by only $\pm 2\%$.[107,108] On the other hand, the formally symmetrical ion $(ClHCl)^-$ is sensitive to its environment.[109]

In contrast to the non-dipolar $(AH)_n$, the strongest interaction with a solvent is undergone by the highly polar dimers AH.B of small molecules (NH_3, CH_3CN, HF, CH_3OH). The wavenumber displacements $\Delta\nu_S$ of these dimers are much greater in the liquid phase, and are sometimes more than twice those for the gas phase, so that the solvation displacement reaches 100–140% of the primary displacement $\Delta\nu^0$, and its absolute magnitude reaches about 500 cm^{-1} (Table 6). Thus the effect of solvation of the H-complex by an aprotic solvent may be greater than the primary effect of H-bond formation. In these cases, the conclusions that the H-complex is independent of the environment and that a local H-bond A–H...B is formed are extremely approximate.

The solvation is stronger, the more polar the partner molecules in the complex and the smaller their size.[95] Thus for the complexes of NH_3 and $N(C_2H_5)_3$ with methanol (Table 6), the displacement $\Delta\nu$ in CCl_4 solution increases by 75% and 25% respectively. The "exposed" ammonia is solvated more strongly than triethylamine, which has undergone "intramolecular solvation". This means, in particular, that the electronic effects of the substituents are greatest in the gas and are levelled out in the liquid, to an extent which is greater, the more active the medium. Thus the picture of the change in the acid–base equilibria in solution examined above (section II) is partly repeated. The factors *P* and *E* characterising the ability to form a H-bond should also depend on the medium, so that, in particular, the proposed[94] extrapolation of the values of *P* and *E* from the solution to the gas is inaccurate. Thus in the gas phase, ammonia is a weaker electron donor than pyridine, whereas in CCl_4 solution the two compounds are comparable in this respect (see $\Delta\nu$ in Table 6), and in a more polar medium, reversal of the relative strengths of these compounds should be expected.

An environment of an H-bond which is similar to it increases its strength by a further factor of 2 compared with that given by the maximum solvation of a polar dimer A–H...B by an aprotic solvent. The change from the free dimer A–H...AH to the polymer $(AH...)_n$ (in the gas or in the liquid) increases $\Delta\nu$ by a factor of 4–6, from 90 cm^{-1} to 300 cm^{-1} and 500 cm^{-1} for methanol and hydrogen fluoride respectively (Table 6); the enthalpy of the H-bond also shows a corresponding increase, from ~3 kcal mol^{-1} in the dimers to 5.5 kcal mol^{-1} and 7 kcal mol^{-1} in the polymers.[83,93,97]

In this long-familiar cooperative effect, which was first proposed to explain the characteristics of liquid water,[110] the group AH, which gives up its proton for H-bond formation, attracts a neighbouring proton more strongly, and by accepting the neighbouring proton it gives up its own proton more readily. Thus charge transfer (polarisation) in a single H-bond AH...A–H partly extends to the sequence $(A–H...)_n$ formed. The effect is extinguished comparatively rapidly along the chain; the frequency ν_S decreases considerably on going from the dimer to the tetramer of an alcohol, and the subsequent multimers are spectrally indistinguishable. The cooperative effect (the non-additivity of the H-bonds) cannot be attributed to the sum of the paired interactions, but the effect is reproduced by calculation of triple interactions.[77] It is the cooperative effect that makes chains of alternating H-bonds such widely encountered structural elements in associated liquids and crystals, in particular those of alcohols and carbohydrates.[83,111]

The contrast between the solvation of polar and non-polar H-complexes indicates additional electrostatic polarisation of the dipolar H-complex by its environment. It resembles the "reactive field effect" in the Onsager model, but probably only outwardly. The only significant interaction is that with the closest solvation layer, which is not characterised by the volume macroparameters of the medium, including the value of ε.

The absolute magnitude of the solvation effect increases regularly with increase in the strength of the H-bond, but changes little relative to the latter.[95] Thus the weak methanol dimer and the strong hetero-dimer $(CF_3)_3COH.NC_5H_5$ in the gas phase are characterised by displacements $\Delta\nu_S$ = 90 cm^{-1} and 900 cm^{-1} respectively, which in solution increase to 150–200 cm^{-1} and 1200–1500 cm^{-1} (Table 6). Further increase in the "polarisation" of AH.B probably leads finally to proton transfer to give the conjugate complex (ion pair) $A^-.H^+B$, and then the separated ion pair $A^-||H^+B$. The values of ΔH also increase regularly,[112] but the changes in the spectrum are not regular, and on the contrary change sign sharply at the hypothetical point corresponding to the "quasi-symmetrical" H-bond A..H...B.[113,114] This phenomenon is not observed in free H-complexes. On the contrary, gaseous hydrochloric acid contains (in addition to free molecules) only the molecular complex $H_2O.HCl$,[74] and, similarly, the vapours over the ionic salts NH_4CN or NH_4Cl contain the molecular complexes $H_3N.HCN$ [114] or $H_3N.HCl$.‡ Intra-complex proton transfer in $H_3N.HCN$ is convincingly excluded by the detection of the semi-deuteriated complex $H_3N.DCN$ in the infrared spectrum in the gas phase (by the usual method).[114] Free associates apparently exist only as the molecular complexes AH.B; ion pairs do not exist in the free form, and are stabilised only by intermolecular interaction with the environment. Each acid AH possibly has its own stability limit or, in other words, proton transfer threshold. Thus hydrogen fluoride retains its proton both in water (pK = 3.45) and in strong bases[96] with a H-bond energy of not less than 15 kcal mol^{-1} (estimated from spectral data[96]). The energies of the H-bonds formed by organic OH acids may also reach 11–15 kcal mol^{-1} before the base is protonated. The proton transfer threshold for HCl, HBr, and CH-acids, however, does not exceed 5–7 kcal mol^{-1}, and molecular complexes of these acids with a higher bond energy are not known.

The energies of solvation of H-bonds can be considered. The enthalpies of dimerisation of carboxylic acids decrease considerably in solution,[83] but this fact cannot be generalised, the conclusion cannot be extended to polar complexes AH.B, and this cannot be regarded as a decrease in the strength of the H-bond in the dimer (as is sometimes done). The decrease in ΔH is due entirely to the solvation of the monomer (see below), and does not contradict what has been said above. The ΔH values measured in different media relate to different states of not only the H-complex but also the "free" partners, and spectral estimates of the H-bond in these media

‡ A C Legon, D J Millen *Chem. Phys. Lett.*, 1988, **147** 484

implicitly assume that there is no change in the state of the free partners; this difference in the states of the products of dissociation of the H-bond must be borne in mind.

The usual notation for complex formation AH + B ⇄ AH.B is applicable only to the gas phase, and does not take account of the influence of the medium. The qualitative model of the effect of the medium S includes two opposed factors: 1) to combine the two solvated partners AH(S) and B(S) into the H-complex it is necessary to "squeeze out" part of the solvation layer of each partner, leading to a decrease in ΔH, and 2) the overall solvation layer "compresses; the H-complex, increasing ΔH in the medium S. The overall effect of the solvent may have either sign, although the former (decrease) predominates most frequently. According to Iogansen,[94] the "desolvation" of the AH molecule involves the replacement of the weak H-bond (H-interaction) with the solvent by a stronger bond with B. The reaction in solution should therefore be described as follows:

$$AH \cdot S + B(S) \rightleftarrows AH \cdot B(S) + S, \quad (9)$$

where (S), as usual, denotes the "S environment" (the interaction B(S) is not taken into account, since there is no specific model). The solvent SD is regarded as a direct participant in reaction (9); it makes an additive (negative) contribution to the enthalpy of the reaction which is proportional to its electron-donor power E_S^0.[94] Appreciable electron-donor power is shown by all compounds up to the extremely inert perfluorohydrocarbons; the noble gases also form H-bonds with strong electrophiles AH (see above). CCl_4, traditionally used in infrared spectroscopy, is far from the most "inert";[115,116] for example, the energy of the H-bond which it forms with HF is ~2 kcal mol^{-1} (ν_S is displaced by 110 cm^{-1}).

Thus according to the model, the decrease in ΔH in solution is related to the fact that complex formation to give AH.B unavoidably breaks down the H-interaction AH.S. The magnitude of the latter is proportional to the product of two independent parameters:[94] the proton-donor power of the acid AH (P_i) and the electron-donor power of the solvent molecule S (E_S^0):

$$\delta_1 \Delta H = 6.4 P_i E_S^0. \quad (10)$$

Eqn. (10) predicts that the solvent will make an additive contribution to the enthalpy of reaction (9). The strength of the H-interaction AH.S can be determined not only using Eqn. (10) but also from the increase in the intensity of the ν_S infrared band in solution (compared with the gas phase AH), determined by "spectral calorimetry".[97] The direct determination of $\delta_1 \Delta H$ by the usual methods is difficult, because of the need to distinguish the "non-specific" interaction.

The increase in the strength of the H-bond of the dimer AH.B as a result of the polarising action of the medium can be estimated only from the ν_S frequencies. The extension to the solvation displacements of the published correlations[97] (which assumes that they are also applicable in the gas phase) leads to the expression

$$\delta_2 \Delta H = 0.055 \delta \nu_s / -\Delta H^0. \quad (11)$$

The accuracy of the prediction (11) must be examined carefully, because of the limitations of the correlations[97] and their "transfer" to the gas; independent data are consistent with Eqn. (11), but are few in number.

If the action of the solvent on an associate is slight, as with $(RCOOH)_2$, Eqn. (10) describes the total effect of the solvent. Thus the changes in $-\Delta H$ for the dimerisation of trifluoroacetic acid in solution, calculated using Eqn. (10) coincide with the measured values (Table 7), that is the H-interaction is the main component of the solvation of the acid monomer; the van der Waals interaction is weak and approximately the same for different solvents (see Table 7). The measured and calculated values of $-\Delta H$ for the dimerisation of other acids in different solvents show similar agreement;[105] in benzene, the energy of solvation of the "free" acid reaches 4 kcal mol^{-1}.

Table 7. Enthalpies of dimerisation and solvation of trifluoroacetic acid in different media, kcal mol^{-1}.

Medium	Dimerisation		Solvation of the monomer	
	measured (Ref.117)	calculated from Eqn. (10)	measured (Ref.117)	calculated from Eqn. (10)[a]
Gas	—	(7.0)[b]	—	—
Cyclohexane	5.8 (3)	5.72	2.3 (4)	1.28
Carbon tetrachloride	4.6 (2)	5.13	3.4 (6)	1.87
Benzene	(3.7)[c]	2.94	5.2 (6)	4.06
1,2-Dichloroethane	3.5 (4)	3.10	5.3 (6)	3.90

[a] Only H-interaction; [b] accepted value; [c] estimated by analogy.[117]

An example can be used to illustrate the increase in the strength of a H-bond in the non-polar CCl_4, or more accurately the positive contribution δ_2 calculated using Eqn. (11) from the experimental frequencies in Table 6. For three typical dimers, namely the non-polar $(RCOOH)_2$ and the polar methanol.ether and (smaller) methanol.ammonia, this increase in strength has values of about 0.3, 0.8, and 1.5 kcal mol^{-1} respectively, or 4, 25, and 40% of the energy of complex formation in the gas phase. With the opposed contribution δ_1, the expected change in $-\Delta H$ is appreciably negative in the first case (Table 7), close to zero in the second, and positive in the third (0.7 kcal mol^{-1}). In polar media, the same increase in the strength of the H-bond δ_2 may be appreciably greater, reaching 60–70%. Finally, the greatest increase in the strength of the H-bond by 3–4 kcal mol^{-1} or more than 100% is observed in an associated liquid, or more accurately a polymeric associate (see above). The results of direct measurements of ΔH in undiluted polar bases in general are consistent with the above spectral estimates. Although data have been obtained for the unique case of self-associates, the most interesting and illuminating data for the highly polar H-complexes of small molecules in different environments have not been obtained.

VI. Summary

Thus the analysis of published data has shown that the variety of theoretical and experimental approaches to the solution of the problem of the influence of the medium on acid–base equilibria not only reveals definite qualitative regularities but also makes it possible to take quantitative account of the influence of specific solvation. Considerable progress in the understanding of the role of hydrogen bonds can be expected from the study of ionic dimers and clusters in the gas phase and in relatively inert media. Further studies of the solvation of neutral H-complexes are required; it may be hoped

that the observed similarity in the influence of solvation on hydrogen bonds and acid–base equilibria will be described quantitatively. Important information on the role of the medium will be provided by a more extensive combination of quantum-chemical calculations for dimers and small clusters with the methods of molecular dynamics and Monte Carlo methods, which make it possible to take account of the contribution of hundreds of solvent molecules.

An important direction of future studies will probably be the development of a single approach to charged and neutral associates. The "complementary nature" of the information makes their comparison difficult; for ion–molecule complexes, a large amount of data has been obtained on their energy of formation, whereas for neutral complexes, a large amount of data has been obtained on their structure and spectral properties.

The task of research workers in physical organic chemistry and various branches of spectroscopy should be to build bridges between acid–base equilibria in the gas phase, molecular and ionic hydrogen bonds, and their solvation in different media.

While the present manuscript was being prepared for publication, a number of new papers which must be included were published.

Data on the energy of anionic H-complexes (O^-, Cl^-, N^-, S^-)[118] and complexes of carbanions,[119] and on their hydration in the gas phase, have been published. Two papers[120,121] have been devoted to the application of previously examined approaches to biological systems (proteins and enzymes). Finally, an experimental and theoretical study of the gas-phase CH-acidity in aromatic and heterocyclic compounds has been carried out.[122]

A linear relationship has been established[123] between the proton and carbon basic strength ($CH_3A \rightarrow CH_3^+ + A^-$) in the gas phase. The observed deviations in an aqueous medium have been analysed. Experimental methods and statistical thermodynamic calculations have been used to study isotopic effects in the hydration of gas-phase ions, and it has been concluded that "light" water coordinates preferentially to both cations and anions.[124] Data have been published[125] on the acidity of a number of radical-cations in the gas phase and in DMSO, and the influence of solvation on the $pK_{HA}^{+\cdot}$ values has been discussed. A method has been proposed[126] for the theoretical calculation of pK_a for organic compounds in water by a combination of non-empirical and Monte Carlo calculations.

Without attempting to list the large number of gaseous complexes for which new studies have been carried out, the development of spectra studies may be noted. These are being extended to multimers (clusters) and in particular to linear homo- and hetero-trimers,[127] where the cooperative effects of two "conjugated" H-bonds A–H...A–H...A–H have been observed. The isomerism of the structure of molecular complexes, that is the two minima of the potential energy of the relative orientation of the partners AH and B, has been more effectively studied. For example, in addition to the T-shaped complex $HCN.CO_2$ with an N...C bond, the less stable complex NCH...OCO has been observed (see the paper by Klots and co-workers[128] and references therein).

In an analysis of accurate spectral data on interatomic distances, Legon and Millen[129] revealed the "course" of the isotopic effect in the H-bond. The replacement of H by D decreases the zero-point amplitudes of hydrogen, both tranverse and longitudinal; the first increases, and the second decreases, the strength of the H-bond (as in the excitation of the vibrations ν_B and ν_S). With increase in the strength of the H-bond, the first contribution, which changes in the same sense as the "flexibility" of the H-bond, decreases, whereas the second, which changes in the same sense as the anharmonicity of ν_S, increases. Thus the overall isotopic effect may change sign: the deuterium bond is stronger than the proton bond for weak H-bonds, but is weaker in the case of strong H-bonds.

The new far infrared laser spectroscopy has demonstrated its promising possibilities in the interpretation of the complex rotational–tunnel spectrum of the water dimer.[130] As a result of the observation of the ν_B vibrations, it is also applicable in principle to cyclic non-dipolar (so that there is no rotational spectrum) associates—dimers and multimers $(AH)_n$.

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Enantioselective effects in coordination compounds

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ABSTRACT. The information that has appeared during the last 15 years relating to enantioselectivity in the formation and reactions of kinetically inert and kinetically labile complexes is classified in the present review. Attention is mainly given to chiral discrimination of ligands that are exchanged in the internal or external coordination spheres of the complexes. The occurrence of enantioselective effects has also been recorded in reactions of coordination compounds that occur without ligand exchange, in particular, in photochemical processes. The variety of forms in which enantioselectivity is displayed is shown and methods for studying it are described.

The bibliography includes 223 references.

Contents

I. Introduction 152
II. Enantioselective effects that accompany ligand exchange in the internal coordination sphere of kinetically inert complexes 152
III. Enantioselective effects that accompany ligand exchange in the internal coordination sphere of kinetically labile complexes 154
IV. Enantioselective effects in kinetically inert and kinetically labile coordination compounds that accompany outer-sphere ligand exchange 157
V. Enantioselective effects in the reactions of coordination compounds that occur without ligand exchange 159

I. Introduction

Enantioselective effects may be encountered in very different regions of chemistry and biochemistry. These are the enantioselective effect of enzymes on racemic substrates, the enantioselective polymerisation of chiral monomers, photochemical processes involving circularly polarised light, etc. The variety of areas in which the reactions of enantiomers have been studied has resulted in the fact that up to the present time no single stereochemical terminology on selective and specific processes has developed. This literature review contains material that is selected in accordance with that definition of enantioselectivity which we gave in our first review[2] devoted to this subject—processes in which one out of the two enantiomeres present in a system is mainly involved are enantioselective. This type of discrimination can naturally only occur in a reaction with a particular chiral reagent (discriminator, selector), so in the general case enantioselectivity is the difference in the reaction of two enantiomeres with some third chiral structure.[1,2]

II. Enantioselective effects that accompany ligand exchange in the internal coordination sphere of kinetically inert complexes

Enantioselective processes that accompany ligand exchange in the internal coordination sphere of kinetically inert complexes were some of the first to be found in coordination chemistry. The most intensive studies of these processes were carried out at the end of the 1960's and the beginning of the 1970's. Enantioselectivity in kinetically inert systems may be both kinetic and thermodynamic in nature and in many cases it is no easy task to separate the contributions of these effects. It is assumed that a state of equilibrium between possible isomers of an inert complex is catalysed by the addition of active carbon, and this method is frequently used to achieve "thermodynamic" enantioselectivity.

Tatechata[3] studied the formation of $[Co(phen)_2(S\text{-aa})]^{2+}$ complexes (phen = phenanthroline, aa = amino-acid) from racemic Δ,Λ-*cis*-$[Co(phen)_2Cl_2]^+$ and *S*-amino acids (Ala, Leu, Ile, Val, and Phe were studied). The resulting diastereomeric complexes were separated by chromatography on Sephadex. The ratio of their Δ- and Λ-isomers was determined. The Λ-isomer was mainly formed in the systems studied, and the enantioselectivity increases significantly with an increase in branching of the α-substituent of the amino acid. Having studied the ^1H NMR spectra of the complexes, Tatechata[3] established that the amino acid in $[Co(phen)_2(S\text{-aa})]^{2+}$ has an equatorial configuration of the α-alkyl substituent. Enantioselectivity occurs as a result of the different degree of nonbonded interactions between the α-alkyl group of the amino acid and the aromatic ligands in Δ- and Λ-structures.

In a series of studies Vagg and Williams[4–11] studied similar reactions for racemic ruthenium complexes Δ,Λ-$[Ru(phen)_2Cl_2]$ or Δ,Λ-$[Ru(bipy)_2Cl_2]$, where bipy = bipyridyl, and since the reaction was carried out using excess *S*-amino acid, no enantioselectivity was found. However, the authors subsequently determined the equilibrium constants for isomerisation of the form:

$$\Delta\text{-}[Ru(am)_2(S\text{-aa})]^+ \rightleftarrows \Lambda\text{-}[Ru(am)_2(S\text{-aa})]^+,$$

where am = bipy or phen. The constants proved to be different from unity. The Λ-diastereomer is more stable for *S*-Phe, *S*-Tyr, *S*-His, and *S*-Pro.[5] At first glance these results do not have any bearing on enantioselectivity. But it follows from them that if the authors had used an insufficient quantity of *S*-amino acid, the Λ-isomer of the initial racemic complex would have mainly undergone reaction with *S*-Trp, *S*-Phe, *S*-Tyr, *S*-His, and *S*-Pro in reaching thermodynamic equilibrium. The reverse pattern would have occurred with *S*-Glu, *S*-Ala, and *S*-Ser.

In a series of studies by Yoshikawa et al.[12–17] the enantioselectivity and enantiospecificity of processes involving the formation of cobalt tetramine complexes was investigated. The coordination of tetramines is stereospecific and the *cis*-β-isomer is

mainly formed, its absolute configuration being clearly (100% enantiospecificity) determined by the optical configuration of the tetramine. For those tetramines studied—3(*S*),8(*S*)-Me_2-trien, 5(*R*)-Me-trien, 2(*S*),10(*S*)-Me_2-trien, 3(*S*),9(*S*)-Me_2-trien, and 1(*R*),2(*R*)-baetchxn, where trien = 1,4,7-triazaheptane, baetchxn = *N*,*N*′-bis(β-aminoethyl)diaminocyclohexane—the optical configuration of the cobalt complex was found to be Λ.[13,14] When this complex coordinates an amino acid molecule on to the two remaining free coordination sites to form $[Co(am)(aa)]^{2+}$, the coordination is again stereospecific with the Λ-β_2-structure mainly formed.

When the amino acid has an *N*-alkyl substituent (*N*-Me-Ala was the most widely studied), with such an amino acid fragment there will be two asymmetric centres in the complex—the carbon atom with a configuration that is determined by the configuration of the amino acid and the nitrogen atom which becomes asymmetric on coordinating. For most of the systems studied coordination of the nitrogen atom of an *R*-amino acid is not enantiospecific and the corresponding diastereomers are in equilibrium (which is rapidly established even at pH 7) in equal quantities. Only in the case of 3(*S*),8(*S*)-Me_2-trien and *N*-Me-Ala is there a ratio of 3:1 for diastereomers with *R*- and *S*-configurations of the N atoms. On the other hand, in complexes with *S*-amino acids the coordination of the N atom is 100% enantiospecific and only the *R*-diastereomer is formed. It was also shown that the ratio of diastereomers (on the nitrogen atom) is independent of the pH of the medium since equilibrium is reached even in neutral solution.[16]

At the same time, racemisation of the asymmetric carbon centre of the amino acid residue occurs in alkaline solution, resulting in the equilibrium:

$$\Lambda\text{-}\beta_2\text{-}[Co(am)(S\text{-}aa)]^{2+} \rightleftarrows \Delta\text{-}\beta_2\text{-}[Co(am)(R\text{-}aa)]^{2+},$$

where *R* and *S* denote the configuration of the C atom of the amino acid. Yamaguchi et al.[17] determined the ratio of the respective diastereomers in the equilibrium solution. These results, just as the results for the Ru complexes reported above, characterise not only the enantiospecificity of the complex formation process but also the enantioselectivity of the reaction:

$$\Lambda\text{-}\beta_2\text{-}[Co(am)]^{3+} + R,S\text{-aa} \rightleftarrows \Lambda\text{-}\beta_2\text{-}[Co(am)(R\text{- or }S\text{-aa})]^{2+}.$$

The enantioselectivity of this reaction depends both on the type of amine and on the structure of the amino acid. The introduction of an *N*-alkyl substituent has a particularly marked influence as does the ability of the α-alkyl substituent of the amino acid to form hydrogen bonds with the nitrogen atoms of the tetramine. The authors consider that the reason for enantioselectivity occurring lies in the difference between nonbonded interactions of both an interligand and intraligand type in the diastereomers. Conformational calculations were carried out in order to determine the most stable conformations of some complexes.[15] According to these calculations, $\{Co[2(S),10(S)\text{-}Me_2\text{-}tet]_2(R\text{-}Ala)\}^{2+}$, where tet = 1,4,7,10-tetraazadecane, is no different in energy from $\{Co[2(S),10(S)\text{-}Me_2\text{-}tet](S\text{-}Ala)\}^{2+}$, but $[Co(S,S\text{-}pyht)(S\text{-}Ala)]^{2+}$, where pyht = 1,7-bis(2-pyrrolidyl)-2,6-diazaheptane, is 3.15 kJ mol^{-1} more stable than $[Co(S,S\text{-}pyht)(R\text{-}Ala)]^{+}$. The latter value is quite close to the difference between the energies of the diastereomers (3.95 kJ mol^{-1}) found experimentally. At the same time, a value of 1.72 kJ mol^{-1} in favour of the diastereomer with (*S*)-Ala was found experimentally for the first system.

Yamaguchi et al.[16] subsequently carried out a more detailed conformational analysis of $[Co(am)(R\text{- or }S\text{-}N\text{-Me-Ala})]^{2+}$ complexes that took into account the contribution from the asymmetric nitrogen atom, and they obtained values for the conformational energy that agreed quite well with the experimental values. This is an indication of the correctness of the chosen model, from which it follows that the main contribution to enantioselectivity in this system is made up by distortions of the torsion and bond angles resulting from nonbonded interligand interactions. The system studied by Yoshikawa et al.[12–17] displays quite a small difference in conformational strain energies for two comparable diastereomers.

In a similar manner Brubaker and Massura,[18] by minimising the energy of nonbonded interactions in cobalt complexes with *N*,*N*′-bis(2-picolyl)-1,2-(*S*)-propylenediamine and alanine enantiomers, found that the difference in conformational strain energies between the two diastereomers was 2.5–3.5 kJ mol^{-1}, and they managed to detect both diastereomeric forms of the complex in an equilibrium solution.

The search for highly selective systems constitutes one of the areas of research on the stereochemistry of coordination compounds. A group of Japanese research workers led by Fujii[19–26] has had considerable success in this field. The authors studied heteroligand complexes of cobalt with Schiff bases and amino acids such as [Co(SB)(aa)], where SB = bis(salicylideneamino)ethylene (sal_2en) and its methyl derivative (Me-sal_2en) or bis(2-hydroxynaphthylideneamino)ethylene ($bsal_2en$). These Schiff bases coordinate stereospecifically with a Co atom to form exclusively the *cis*-β_2-structure.[19] Subsequent reaction of $[Co(sal_2en)]^{+}$ or $[Co(Me\text{-}sal_2en)]^{+}$ complexes with an *S*-amino acid (the reaction is carried out until thermodynamic equilibrium is reached) results in the formation of two diastereomers in unequal proportions; the ratio varies from 1.5:1 for *S*-Ala to 17:1 for *S*-Trp in favour of the $(-)_{435}$-diastereomer.[20] Correctly assuming that if racemic amino acid and optically active complex were reacted separation of the racemate could be achieved, Fujii et al.[21,22] used the enantiospecific coordinating ligand (1*S*,2*S*)-*N*,*N*′-1,2-cyclohexane-bis(salicylideneamine) (sal_2chxn), which forms complexes exclusively with a Λ-β_2-structure, in this reaction. In this case they achieved the following degree of enantiomeric enrichment remaining in the excess amino acid: Ala 6–8% (*R*), Leu 6–8% (*R*), Met 6–8% (*R*), Ser 10–12% (*R*), Thr 27–30% (*R*), Asp 16–18% (*R*), Glu 6–8% (*R*), Phe 39–41% (*R*), Trp 41–43% (*R*), Pro 48–50% (*S*). The results obtained agree quite well with the data from the determination of thermodynamic enantioselectivity in the same complexes in dimethylformamide:water (1:4) solution,[23] where the structure containing the *S*-enantiomer of the amino acid (Ala, Val, Leu, Phe, Trp were studied) proved to be the most stable. Thus, the Λ-complex preferentially contained an *S*-amino acid. Only proline, whose *R*-enantiomer proved more active, constituted an exception.

In this connection the [Co(Me-sal_2en)(*S*-Pro)] system was studied in greater detail.[24] It was found that when starting from *S*-proline and $[Co(Me\text{-}sal_2en)]^{+}$ the less stable diastereomer, which has a negative rotation at 435 nm, is initially formed, but subsequently it is slowly converted to the $(+)_{435}$-diastereomer. The rate constant of isomerisation *k* is equal to 7.95×10^{-5} s^{-1},[24] and according to the ^1H NMR spectra, only one isomer is present in the final solution. A similar transformation was subsequently also found for [Co(Me-sal_2en)(*S*-Hyp)] and [Co(Me-sal_2en)(*S*-*a*-Hyp)]. The degree of kinetic enantioselectivity, determined from the ratio of diastereomers $(-)_{435}$:$(+)_{435}$ at the initial moment in time, was lower in these complexes (56% for *S*-Hyp and 23% for *S*-*a*-Hyp) than for proline (87%).[25] However, in this case, just as for proline, a gradual conversion to the more stable $(+)_{435}$-diastereomer occurs.

Fujii et al.[26] subsequently succeeded in finding a system in which kinetic enantioselectivity occurs for other amino acids, in particular for valine and isoleucine. $[Co(bsal_2en)]^+$ complexes had this property. A considerable effect from the solvent on the ratio of diastereomeric structures in solution was reported.

The *N*-alkyl substituent in the amino acid residue of the complex has a very considerable effect on the degree of enantioselectivity. Thus, if the complex $[Co(Me\text{-}sal_2en)]^+$ is reacted not with *S*-alanine (ratio $\Lambda/\Delta \approx 2$) but with its *N*-methyl derivative, the content of Λ-isomer in the equilibrium mixture is as high as 93% while for the *N*-benzyl derivative it is 100%.[19] Correspondingly, if Λ-*cis*-β_2[Co(*S*,*S*-sal$_2$chxn)]$^+$ is used, racemic *N*-benzylalanine reacts with almost 100% enantioselectivity, leaving the *R*-enantiomer unreacted. The ratio of the resulting complexes for the system [Co(Me-sal$_2$en)(*R*- or *S*-*N*-Bzl-Ala)] was used to establish the following relative stability of diastereomeric complexes (configuration of the complex, configuration of the N atom in the amino acid molecule, and configuration of the amino acid are given): $\Lambda(S,S) = 19.5$; $\Delta(R,S) = 11.3$; $\Delta(S,S) = 8.2$; $\Lambda(R,S) = 0$ kJ mol^{-1}. This corresponds to the following ratio of $\Delta(R,S):\Delta(S,S)$ diastereomers at equilibrium of 96.5 : 3.5.[11] For comparison we can indicate that for the {Co[3(*S*),8(*S*)-Me$_2$-trien](*N*-Me-Ala)}$^{2+}$ system reported above the three complexes $\Lambda(R,S)$, $\Delta(S,S)$ and $\Delta(R,S)$ are in equilibrium in the ratio 60 : 20 : 20, which corresponds to a considerably lower selectivity for the system.

The high enantioselectivity for formation of complexes based on quadrivalent Schiff bases was also confirmed by Okawa,[27] who synthesised complexes of cobalt with Schiff bases obtained from 1,2-diaminopropane or *trans*-1,2-diaminocyclohexane and 1(*S*)-menthyloxy-3-benzeneacetone. If a Schiff base obtained from a racemic diamine is reacted, there is the sole formation of the Λ-*cis*-β_1-structure of the complex, containing only *R*-propylidenediamine or *S*-cyclohexanediamine residues.

The enantioselectivity found in complexes of cobalt with trimethylene-bis(pyrrolidine-2-carboxylic acid) is just as high.[28] This ligand coordinates enantiospecifically and stereospecifically, giving an asymmetric Λ-structure. Subsequent reaction of this complex with *R*,*S*-proline or *R*,*S*-pipecolinic acid results in the formation of a heteroligand complex that contains only the *R*-enantiomers of the amino acids.

The majority of the studies described above had octahedral complexes of trivalent cobalt as the subject of their research; these complexes were and remain a favourite topic in stereochemical studies. At the same time other kinetically inert complexes, and particularly other coordination polyhedra, in relation to enantioselectivity remain almost unstudied. There is no doubt that the study by Payne and Stephan[29,30] on square planar platinum complexes proved very interesting in this respect. Complexes with this type of stereochemistry were regarded as unfavourable subjects for the study of enantioselectivity. Since the ligands in these structures are situated at a considerably greater distance from each other compared to octahedral complexes, the occurrence of interligand interactions — the basis of enantioselectivity — seemed improbable. However, this study disproved these predictions. Platinum complexes that contained a chiral diphosphine ligand, methyl group, and chlorine atom reacted with a racemic monoamine or monophosphine to give diastereomers in a ratio which quite frequently differed from 1 : 1, which was an indication of the enantioselective course of the reaction.

Equally, Shinoda et al.[31] found that for the reaction of *trans*-{Pt(Cl$_2$)(SR$_2$)[(*R*,*S*)-Val-OMe]} with *R*- or *S*-phenylethylamine there were quite noticeable differences in the equilibrium constants, which indicate the preferential replacement by phenylethylamine of the amino acid ligand belonging to a configurational series opposite to that of the amine itself.

Studies on enantioselectivity in reactions of organometallic compounds should also be mentioned. Although research into the preparation of diastereomeric organometallic compounds was started a long time ago (see, for example, the study by Brunner[32] and the references in it), the question of the ratio of concentrations of the resulting diastereomers or the ratio of their rates of formation has generally not been raised. In the studies of Kane-Maguire et al.[33–35] it was shown that $[Fe(CO)_3(1\text{-}5\eta\text{-}2\text{-}MeOC_6H_6)]^+$ reacts with optically active phosphines[33,34] or phenylethylamine,[35] exhibiting both kinetic and thermodynamic enantioselectivity. Pearson and Yoon[36] reported that the reaction of iron dienyl complexes of the type $(\eta^4\text{-COD})Fe(CO)_2[P(OEt)_3]$ with optically active enolates stabilised with sulphoximine is enantioselective (about 50% enrichment) and may be used to obtain an organometallic derivative in an optically active form. They noted a considerable effect of the nature of the enolate cation on the degree of enantioselectivity (Li exhibits a considerably lower enantioselectivity than K).[36] A system in which the enantioselectivity is close to 100% is described in a study by Tsyryapkin et al.[37] The reaction of racemic $[Mn(CO)_3(\eta^5\text{-}1\text{-}N\text{-}Me_2\text{-}2\text{-}CHO\text{-}C_5H_3)]$ with optically active dipeptides in the presence of Cu^{2+} ions takes place in such a manner that only the $(-)_{435}$-enantiomer of the complex forms a Schiff base, while the $(+)_{435}$-isomer remains unreacted and can be isolated by extraction from the reaction mixture. Subsequent study of this reaction showed that the enantioselectivity depends to a considerable degree on the structure of the dipeptide.[47] Thus for Gly-(*S*)-Ala the ratio of diastereomeric complexes is 41 : 1 but for (*S*)-Ala-Gly or (*S*)-Val-Gly it is close to the statistical average.

It was found quite unexpectedly that organometallic compounds can act as substrates for enzyme reactions.[39] Although the enantioselectivity of the hydrolysis of (2-ethoxycarbonylbuta-1,3-diene)iron tricarbonyl with pig liver esterase was not so high (an optical purity of about 85% for the acid isolated), with a subsequent single-stage crystallisation a product with an optical purity of >98% could be obtained.

III. Enantioselective effects that accompany ligand exchange in the internal coordination sphere of kinetically labile complexes

In contrast to kinetically inert complexes with an octahedral structure, kinetically labile complexes did not originally attract a great deal of attention from research workers. The two main reasons for this situation may be stated here. Firstly, the majority of kinetically labile complexes have a square planar or tetrahedral structure of the coordination polyhedron which were not considered conducive for the display of enantiomeric effects. Secondly, in contrast to kinetically inert complexes, where each diastereomer can be isolated and characterised in a pure state, with kinetically labile complexes the researcher is compelled to work with an equilibrium mixture of all possible forms, whose individual properties can only be obtained by calculation. This naturally complicates the investigation.

The increased interest in this class of coordination compounds is due to the development of ligand-exchange chromatography,[1] which is based on the use of enantioselective effects in labile systems.

Even in the initial studies carried out by Davankov et al.[2] relating to the simulation of processes in ligand-exchange chromatography, considerable enantioselective effects were found in square planar complexes of Cu^{2+} with bidentate *N*-alkyl-α-amino acid ligands.[2] These investigations were subsequently extended in studies by other scientists.

Ritsma[40] studied bis-complexes of bivalent Co, Ni, Cu, and Zn with *N*-(*o*-hydroxybenzyl)alanine. From his results it is clear that the addition of a second ligand (chiral amino acid) to the metal is enantioselective. In the case of Co and Ni the formation of structures that contained ligands of the same optical configuration proved more favourable. Ritsma accounts for the occurrence of enantioselectivity by the fact that Co and Ni ions form octahedral complexes. On the other hand, in Cu complexes (square planar configuration) or Zn (tetrahedral configuration) there was no enantioselectivity. The difference between the stability constants of log 0.3 reflects only a statistical preference for the *meso* structure compared with an equal-paired one.

Ritsma subsequently studied[41] a further series of tridentate amino acid ligands: histidine, α-*N*-methylhistidine, α-*N*,*N*-dimethylhistidine, α-*N*-benzylhistidine, aspartic acid, glutamic acid, and their complexes with Co(II), Ni(II), Cu(II), and Zn(II) ions. In this case enantioselectivity was found not only for octahedral Co(II) and Ni(II) complexes but also for some Cu(II) and Zn(II) complexes. Moreover, as detailed studies of copper complexes showed,[40] enantioselectivity depends to a considerable extent on whether the amino group of histidine is protonated or not; protonation causes a change in enantioselectivity so that the formation of an equal-paired structure is preferred.

These results were subsequently confirmed by Pettit et al.[42] In a potentiometric study of the stability of complexes of Co(II), Zn(II), Ni(II), Pb(II), and VO(II) with histidine in unprotonated complexes, enantioselectivity was only found for Co, Ni and Zn, but in monoprotonated complexes it also occurred for Cu.

The study of histidines was extended by Pettit[43] to imidazolyl-substituted derivatives. In the ternary complexes M(*N*-imidazolyl-substituted histidine)(*R*- or *S*-histidine), the formation of M(*R*)(*S'*) complexes was more favourable for Ni and Zn. For Cu there was no enantioselectivity in the unprotonated complex while in the monoprotonated complex formation of an M(*R*)(*R'*) structure was more favourable.

However, in studies on ternary complexes containing histidine (or its *N*-substituted derivative) and bidentate amino acid ligands, results were obtained that differed from those described above. In this case selectivity occurred as a rule in unprotonated complexes but in protonated complexes it was absent.[44–46] Moreover, substituents in the imidazole ring affected the degree of enantioselectivity much less than did substituents on the α-amino group. An even more unexpected result was that there was no enantioselectivity in the analogous Ni(II) complexes.[45] It was also not found in heteroligand complexes of copper with histidine when the second amino acid ligand was threonine, serine, proline, or methionine.[46]

In order to elucidate the mechanism of enantioselectivity, Pettit et al.[45,47,48] undertook a potentiometric study of ternary complexes of bidentate amino acids. In most of the systems studied the enantioselectivity was insignificant or absent but for the system Cu–proline–tryptophan the Cu(*S*)(*S'*) structure proved more stable than the Cu(*R*)(*R'*) complex by a factor of log 0.26.[45]

For complexes of Cu with serine and threonine there is very little difference between the stability constants of the diastereomeric structures but, on the other hand, there is a distinct difference in the enthalpy of formation of these structures, as determined by calorimetry.[47] The Cu(*R*)(*R'*) structure was preferred. However, its enthalpy advantage is completely balanced by the entropy contribution, so the free energies of formation of *meso* and equal-paired structures become the same. A similar ratio of enthalpy and entropy contributions in the formation of *meso* and equal-paired structures of the complexes was also found in the system Cu-*N*-benzylproline.[49] But there was not a complete balance of the contributions in this system and as a result of the predominance of the entropy contribution, the formation of a *meso* structure was preferred. At the same time, in a complex of Ni(II) with methionine both the enthalpy and entropy contributions favour the formation of a *meso* structure; it proves to be 2.72 kJ mol^{-1} more stable than the equal-paired structure.[48]

With an improvement in the process for calculating the stability constants of complexes and methods for studying equilibrium systems, research workers have repeatedly directed their attention to complexes of copper(II) with bifunctional α-amino acid ligands, trying to find enantioselectivity in this most simple system. Thus, Olin et al.[50–52] again studied the formation of complexes with optically active and racemic ligands for the following α-amino acids: valine,[50] proline, serine, threonine, tryosine,[51] and aspartic acid.[52] In the majority of the systems, according to the findings of earlier studies,[2] enantioselectivity was not found, but for valine and tyrosine complexes it was possible to detect slight enantioselectivity. In the case of valine the equal-paired structure was preferred (log β_2^{RR} = 14.698, log β_2^{SS} = 14.699, log β_2^{RS} = 14.690), while in the case of tyrosine the meso structure was preferred (log β_2^{RR} = 14.355, log β_2^{RS} = 14.360). However, the differences occurring in this case probably lie within the limits of experimental error for determination of the constants.

Enantioselectivity was recorded with much greater reliability in a study of heteroligand complexes of proline with a number of other bidentate amino acid ligands,[53] where formation of a Cu(*S*)(*S'*) structure proved to be more favourable. As was mentioned above,[45] enantioselectivity of the same sign was also found in a complex of copper(II) with proline and tryptophan, so that this effect can be regarded as typical in proline complexes. From this point of view, and this was stressed by Olin et al.,[53] it is surprising that there is no enantioselectivity in the homoligand bis-complex of proline with Cu(II).

Sakurai et al.[54–56] tried to detect enantioselectivity in copper complexes that contained amino acids with functional groups carrying different electrical charges or forming hydrogen bonds between themselves. It was suggested that in one of the diastereomeric structures of the complex, interactions between the functional groups will occur more readily than in the other. The systems copper(II)–(aspartic acid or glutamic acid)–(lysine, ornithine, or asparagine),[54] copper(II)–(histidine)–(asparagine, homoserine, glutamine, citrulline, serine, threonine, alanine, or valine)[55,56] were studied, but enantioselectivity was not found at all. The resolution of the amino acid enantiomers that occurs on crystallisation of the ternary complexes[57–59] is probably due to the enantioselectivity of the process for crystallising diastereomeric salts, which has been known since the time of Pasteur.

It should be mentioned that in other studies[60,61] enantioselectivity was in fact found in a system of ternary complexes containing histidine and an amino acid ligand. For diaminocarbonyl ligands the formation of complexes containing ligands of a single

configurational series was more favourable,[60] while for a Zn(histidine)(threonine) complex the Zn(*S*-His)(*R*-Thr) form was more stable.[61]

Angelici et al.[62] studied enantioselectivity in complexes of Co(II), Ni(II), Cu(II), and Zn(II) with β-(2-pyridyl)-α-alanine and β-(6-methyl-2-pyridyl)-α-alanine, regarding them as analogues of the histidine ligand. They found that for Co(II), Ni(II), and Zn(II) the formation of *meso* structures was more favourable (difference in stability constants of the diastereomers reaches almost log 1), while for Cu, as in the case of histidine, there is no enantioselectivity. The authors also showed that introduction of a methyl substituent into the pyridine part of the ligand molecule reduces the difference in stability between the diastereomeric forms of the complexes. They attribute this effect to the reduction in coordinating ability of the 6-methyl-substituted pyridine compared to the unsubstituted ligand.

No appreciable selectivity was found either in the formation of heteroligand complexes of copper(II) with *N*-carboxymethyl-β-(2-pyridyl)-*S*-α-alanine and valine. On the other hand, in ternary complexes of nickel with the pyridyl ligand, noticeable differences in the stability of diastereomers occurred for a whole series of amino acids (ratio of log K_2^{RS} to log K_2^{SS} was 0.25:1 for Ala, 0.21:1 for Ser, 0.56:1 for Val, and 0.26:1 for Phe).[63] The different behaviour of the copper and nickel complexes was attributed to the different structure of the coordination polyhedron in these metals — square planar in Cu(II) and octahedral in Ni(II).

Enantioselective formation of complexes often has an effect on the course of processes that take place in coordination compounds. Kitagawa et al.[64] described nickel complexes with 1,2-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane and its *N*-methyl-derivative that had the ability to catalyse enantioselectively the hydrolysis of α-amino acid methyl esters. At the same time these complexes were able to coordinate enantioselectively amino acid ligands, where in the case of the unsubstituted ligand *R*-enantiomers of alanine and valine were more strongly bonded while in the case of the *N*-methyl derivative it was the *S*-enantiomers of these amino acids and also proline that were more strongly bonded.[64,65] Kitagawa et al.[64,65] noted that there is a direct correlation between the enantioselectivity of the amino acid ligand coordination and the enantioselectivity for hydrolysis of their methyl esters. A similar mechanism for enantioselectivity also occurred for a copper complex of 2-[hexadecyl-*N*,*N*-(2-hydroxypropyl)aminomethyl]pyridine.[66] Micelles formed by this complex were used as a catalyst for the hydrolysis of *p*-nitrophenyl esters of amino acids. The authors maintain that by using micelles they were able to achieve a more than tenfold difference in the rates of hydrolysis of the enantiomers.

In a number of studies[1,67–86,90–95] investigation of enantioselective effects was carried out directly in conjunction with ligand-exchange chromatography. The authors tried to establish a relationship between the degree of enantioselectivity in forming model complexes in solution and the exit order of enantiomers in ligand-exchange chromatography of corresponding racemates on a chiral sorbent. Such studies were first carried out by Davankov et al.[1] in the case of copper complexes of *N*-benzylproline which simulated the coordination compounds formed in the sorbent phase that was obtained from a chloromethylated polystyrene matrix and proline. Subsequently Kurganov et al.[67–73] studied a large number of homo- and hetero-ligand coordination compounds of copper with α-amino acid,[67–70] 1,2-diamine,[71,72] and 1,3-dicarbonyl[73] types of ligands and demonstrated that enantioselectivity occurs in a number of systems. This included the detection of enantioselectivity for the first time in complexes containing diamine ligands.

Considerable attention was given in the studies of Kurganov et al.[67–83] to the mechanism for the occurrence of enantioselectivity. With this purpose the circular dichroism spectra of these coordination systems were studied in detail,[67,73–80] the molecular structures of a number of model complexes were established,[81,82] and a conformational analysis of complexes of copper with alanine and its *N*-methyl derivative was carried out.[83] It follows from conformational calculations[83] that in equilibrium solution as methyl derivatives are introduced on to the nitrogen atom in the ligand molecule the proportion of complexes with a *trans*-structure of the chelate bonding increases and the proportion of *cis*-structures decreases; so for *N*,*N*-dimethylalanine the latter can be ignored. At the same time the difference in conformational energy between the respective diastereomeric forms of the complexes increases in favour of the structure that contains ligands of a single configurational series. These results are in good agreement with the data of crystallographic studies in which both *trans*- and *cis*-structures were found for unsubstituted ligands (amino acids or diamines) but for *N*-alkyl derivatives all of the structures studied were of the *trans* type.[81,82] At the same time, calculated results should be supplemented with data on the entropy component of free energy since, as was mentioned above, the enthalpy (one of the components of which is the conformational energy) and entropy often provide opposing contributions to the total enantioselective effect.

Similar calculations were carried out by Simeon et al.[84–86] for a wide range of conformers of copper(II) complexes with *N*,*N*-dimethylvaline or *N*,*N*-dimethylleucine (only the *trans*-structure of the chelate bonding was considered). According to their results each chelate ring (for example, *N*,*N*-dimethylvaline) has six local minima of conformational energy, one of which lies considerably apart ($\approx$10 kJ mol^{-1}) from all the others (this conformation is similar to that used in calculations on *N*,*N*-dimethylalanine complexes[83]). If the chelate rings are considered to be independent, a copper bis-complex of this ligand can exist in the form of 21 conformers, from which only three display noticeable enantioselectivity, all three containing the above-mentioned minimum-energy conformation at least for one of the chelate rings. The maximum enantioselectivity occurs for conformers in which both rings are in this favourable conformation. However, while for a complex containing *R*,*S*-ligands 98% of the conformers belong to this type, in complexes with *R*,*R*-ligands only 70% of the complexes have such a conformation since the conformational range is substantially greater in them than in complexes with *R*,*S*-ligands. This slightly reduces the enantioselectivity for the preferred formation of a *meso* structure.

From a detailed analysis of the structure of complexes and equilibria occurring in solution, it was later possible for Davankov et al.[87] to formulate a number of general rules for enantioselectivity to occur in square planar complexes with bidentate organic ligands. At the same time there was shown to be no clear correlation between the enantioselectivity of complex formation in solution and the enantioselectivity for separation of enantiomers by ligand-exchange chromatography in related systems. The reason for this proved to be that interactions between the complexes and the achiral stationary chromatographic phase play an active role in determining the enantioselectivity of chromatographic separation.[88] This follows from such an obvious example as the reversal in sign of enantioselectivity of the chromatographic system containing the same

chiral resolving agent and enantiomers being separated by simply changing the type of achiral stationary phase.[88] Moreover, it transpired that chromatographic separation of enantiomers is only possible when the enantioselectivity for the formation of complexes with a chiral selector in solution and on the surface of the stationary phase are different in magnitude (or even better, different in sign).[89]

In more recent studies[90–95] it was suggested that there must be a correlation between the enantioselectivity of formation of model complexes in solution and the enantioselectivity of a chromatographic system. Thus, Tsuchida et al.[90] compared the enantioselectivity of complex formation in the system Cu(II)–(*N*-benzyl-*S*-leucine)–(alanine, valine, or leucine) with the enantiomeric separation of these amino acids on a chiral sorbent obtained by the reaction of *S*-leucine with a chloromethylated copolymer of styrene and divinylbenzene. French research workers[91–95] examined systems of complexes that simulated sorbents, obtained by the reaction of *S*-proline with chloromethylpolystyrene[91,92] or polyacrylamide[93,94] and *S*-phenylalanine with chlorosulphonated polystyrene.[95] In a number of cases qualitative agreement was obtained between the exit order of the enantiomers from the chromatographic column and the enantioselectivity of complex formation in model systems. In the cases where it was absent the authors suspected that the models used were inadequate. In actual fact a model cannot be adequate if it does not transmit the essential adsorptive interactions between the diastereomeric complexes and the achiral surface or matrix of the sorbent.[88,89]

Enantioselectivity in labile complexes with other types of ligands has been studied much less than for amino acid ligands. Pettit and Swash[96] studied the enantioselectivity of complex formation between $[VO]^{2+}$ and tartaric acid ($tartH_2$). They found quite a large number of polynuclear structures in this system, from which a noticeable difference in the stability complexes with racemic and optically active ligands was only found for $[VO]_2(tart)_2(OH)_4$. The structure containing two ligands with opposing optical configurations is more stable.

The same type of relationship of the stabilities of diastereomeric structures of complexes was found for coordination compounds of Cu(II) with tartaric acid.[97] In this case the complex Cu(*l*-tart)(*d*-tart) is approximately twice as stable as the Cu(*l*-tart)$_2$ complex. While enantioselectivity is insignificant for hydroxo complexes present in the system, equal-paired structures are more stable for polynuclear structures with the composition $Cu_2(tart)_2$, the difference in the stability constants being so great (4×10^8 and 0.2×10^8) in an equilibrium solution of a racemic ligand, complexes with the composition Cu_2(*l*-tart)(*d*-tart) are virtually absent (less than 1%).

Petit-Ramel et al.[98] found enantioselectivity in the formation of heteroligand complexes of copper(II) with *N,N'*-dimethyltartramide and mandelic acid. In this case the complex containing *d*-tartaric acid amide and *l*-mandelic acid proved to be more stable (log β_{111} = 17.78). The stability constant of the complex containing *d*-tartaric acid amide and *d*-mandelic acid was lower by a factor of log 0.72.

The reasons for enantioselectivity to occur in these systems, which have a large number of various polynuclear forms, were examined by Tapscott.[99] He wrote a review[100] of the studies on complexes of tartaric acid, in which there is a section devoted to enantioselectivity and a discussion on the thermodynamics of the disproportionation of the complexes $(VO)_2$(*l*-tart)$_2(OH)_4$ and $(VO)_2$(*d*-tart)$_2(OH)_4$ to $(VO)_2$(*l*-tart)(*d*-tart)$(OH)_4$.[101] The enthalpy of this reaction is equal to 1.46 kcal mol^{-1}, which is an indication of the greater stability of the *meso* structure, with a content of not less than 96% in the equilibrium solution, compared to the equal-paired form.

The enantioselectivity of formation of gadolinium and dysprosium complexes with the tartaric acid analogue—α-hydroxysuccinic acid—was studied.[102] The stability constant of the complex with an optically active ligand was less than the stability constant of the complex with racemic hydroxysuccinic acid. Enantioselectivity occurs here in the formation of tris- as well as bis-complexes.

In contrast to α-hydroxysuccinic acid, *O*-phosphoserine did not show any noticeable enantioselectivity in complex formation with Co(II), Ni(II), or Cu(II), but for Zn(II) the equal-paired structure proved more stable than the *meso* structure (by a factor of log 0.28).[103] Enantioselectivity was found[104] in the coordination of histidine with the complex triaqua-tribenzo[*b,f,j*][1.5.9]triazacyclodecylnickel(II). The respective constants for formation of ternary complexes for *S*-His and *R*-His were 7.26 and 7.42. By using this difference in the stability of the heteroligand complexes, Erno and Jordan[104] were able to separate the initial homoligand complex into optical isomers and use it subsequently for the resolution of racemates of a number of other amino acids. However, in the latter case successful resolution is only achieved when two or three recrystallisations of the heteroligand complexes are used, and therefore the question of enantioselectivity occurring in them cannot be regarded as conclusive.

IV. Enantioselective effects in kinetically inert and kinetically labile coordination compounds that accompany outer-sphere ligand exchange

Enantioselective effects of outer-sphere complex formation are known in the chemistry of coordination compounds as the Pfeiffer effect (PE).[105–107] The latter first observed the following phenomenon: there is a change in the angle of rotation of (+)-α-bromocamphor-π-sulphonic acid when it is added to a solution of a racemic $Zn(phen)_3$ complex.[108] With the development of chiro-optical methods for studying PE, circular dichroism spectroscopy started to be used instead of optical rotation measurement.

The first explanation for PE was given by Dwyer,[109] who proposed that in placing a racemic compound in an optically active medium, the equilibrium between the enantiomeric forms is displaced in favour of one of them. He noted at the same time that associates (outer-sphere coordinate compounds) also contribute to PE, those involving enantiomers of the complex and an optically active component of the solution. The resulting associates are no longer enantiomeric but diastereomeric and hence they can have an unequal stability and occur in solution in unequal quantities. Moreover, their molar chiro-optical properties also cannot have the same absolute value.

A further reason for PE was disclosed by Mason,[110] who showed that electronic transitions not only for racemic complexes (i.e., chiral by nature) but also for achiral compounds can be optically active from the effect of a chiral medium. This effect was found by him in the case of the complex $[Co(NH_3)_6]^{3+}$ in a solution of tartaric acid. The extensive occurrence of this phenomenon was subsequently demonstrated.[111–114]

By correlating the results of different authors, Schipper[107,115] proposed two main mechanisms for the occurrence of PE:

associative and nonassociative (inductive). The latter, in essence, is similar to the chiral induction mechanism of Mason. The associative mechanism, according to Schipper, involves three types of equilibria:

$$\Delta\text{-antipode} + S\text{-inductor} \rightleftarrows \Delta\text{-antipode}.S\text{-inductor} \quad (1a)$$
$$\Lambda\text{-antipode} + S\text{-inductor} \rightleftarrows \Lambda\text{-antipode}.S\text{-inductor} \quad (1b)$$
$$\Delta\text{-antipode}.S\text{-inductor} \rightleftarrows \Lambda\text{-antipode}.S\text{-inductor} \quad (2)$$
$$\Delta\text{-antipode} \rightleftarrows \Lambda\text{-antipode} \quad (3)$$

The first of these equilibria represents the formation of diastereomeric associates, while the second and third represent a displacement of the equilibria between associates or enantiomers. All of these equilibria occur simultaneously:

$$\begin{array}{ccc} \Delta + S & \overset{(1a)}{\rightleftarrows} & \Delta\cdot S \\ {\scriptstyle(3)}\downarrow\uparrow & & \downarrow\uparrow{\scriptstyle(3)} \\ \Lambda + S & \overset{(1b)}{\rightleftarrows} & \Lambda\cdot S\,. \end{array}$$

The following equilibrium constants relate to these processes:

$$K^{1a} = \frac{[(\Delta\cdot S)]}{[(\Delta)]\,[(S)]},\quad K^{1b} = \frac{[(\Lambda\cdot S)]}{[(\Lambda)]\,[(S)]},$$
$$K^{2} = \frac{[(\Lambda\cdot S)]}{[(\Delta\cdot S)]},\quad K^{3} = \frac{[\Delta]}{[\Lambda]}.$$

In the case of kinetically labile complexes the equilibria are established rapidly and the observed PE is the total result of all these processes. For kinetically inert complexes the situation is complicated by the slowness in establishing equilibrium and the occurrence of additional kinetic enantioselective effects. On reaching equilibrium, the relationship $K^{1b}/K^{1a} = K^3/K^2$ will be fulfilled for all types of coordination compounds. Thus, PE can be characterised either by the difference in the stability constants of the resulting diastereomeric adducts or by the difference of the epimerisation constant of the resulting adduct from unity (the racemisation constant of the enantiomers). The latter case, according to Dwyer,[109] indicates the shift in chiral equilibrium between enantiomers in an optically active medium.

The occurrence of PE is usually monitored from the change in chiro-optical properties of the system, namely, from the change in angle of rotation or solution ellipticity of the chiral inductor in the presence of a coordination compound. In general, in accordance with the scheme given above, the chiro-optical property of an equilibrium solution can be represented in the following manner:[116]

$$\alpha = \alpha_S[S] + \alpha_\Delta([\Delta] - [\Lambda]) + \alpha_{\Delta\cdot S}[\Delta\cdot S] + \alpha_{\Lambda\cdot S}[\Lambda\cdot S], \quad (4)$$

where α_S, α_Δ, $\alpha_{\Delta\cdot S}$, and $\alpha_{\Lambda\cdot S}$ are the molar characteristics of the chiro-optical properties of the inductor, complex, and adducts respectively.

By analysing equation (4), Ogino and Kumagai[116] came to the conclusion that PE can occur even when there is no redistribution in the concentrations of enantiomers (i.e., $K^{1a} = K^{1b}$) or the chiro-optical properties of the diastereomeric associates appear to be enantiomeric ($\alpha_{\Delta\cdot S} = -\alpha_{\Lambda\cdot S}$). Usually these values differ from each other and the observed PE constitutes the change in chiro-optical properties of the solution both from the change in concentrations of the optically active components already in solution and from the appearance of new ones.

Mason et al.[117] studied PE in a system of racemic complexes $M_3[Cr(ox)_3]$ (ox = oxalate) in optically active esters of α-hydroxy-acids and found that the complex undergoes "antiracemisation" to the extent of 70% whatever the type of M and the configuration of the ester. The effect is completely eliminated by the addition of an equivalent of a crown ether to the solution. Miyoshi et al.[118,119] interpreted PE in a similar manner for $[Co(ox)_2(phen)]^-$ [118] or $[Cr(ox)_3]^{3-}$ and $[Co(phen)_3]^{3+}$ [119] complexes in solutions of quinine, quinidine, cinchonidine, or their derivatives. The same authors studied PE in the case of $[Cr(ox)_2(phen)]^-$ and $[Cr(ox)_2(dipy)]^-$ complexes in the presence of *N*(1)-methyl and 9-acetyl derivatives of the same alkaloids.[120] They showed that the magnitude of the shift of the chiral equilibrium mainly depends on the configuration of the C(8) and C(9) atoms of the alkaloid and that it is greater for acetyl derivatives than for unsubstituted alkaloids. Out of the complexes studied the greatest shift was achieved in $[Co(ox)_2(phen)]^-$ in the presence of 9-acetoxyquinidine (28.3% of enrichment with the Λ-isomer), 9-acetoxyquinine (22.4% of enrichment with the Δ-isomer), and *N*(1)-methyl-9-acetoxyquinine (23.8% of enrichment with the Δ-isomer). The rate constants of racemisation of the Δ- and Λ-isomers of $[Co(ox)_2(phen)]^-$ were also determined in the presence of the same alkaloids, and it was shown that an accumulating isomer in this system had a lower rate of racemisation. Miyoshi et al.[121] demonstrated the possibility of using coordination compounds as a chiral inductor and examined in detail PE for $[Co(ox)_3]^{3-}$ in the presence of optically active *cis*-[M-diamine)$_2$(X)(Y)] complexes, where M = Cr or Co; diamine = ethylenediamine (en) or diethylenetriamine (tr); X, Y = Cl^-, NH_3, NO_2^-, $C_2O_4^{2-}$, and acac. In order to confirm the possibility of a shift in the equilibrium between Δ- and Λ-enantiomers of $[Co(ox)_3]^{3-}$, the authors determined the rate of their racemisation in the presence of $[Co(en)_2(NO_2)_2]$Br enantiomers. Since the rate of racemisation in the Δ−Δ-system proved to be somewhat lower than in the Δ−Λ-system, the authors assumed that in a solution of Δ,Λ-$[Co(ox)_3]^{3-}$ when Δ-$[Co(en)_2(NO_2)_2]$Br is added, Δ-$[Co(ox)_3]^{3+}$ will accumulate. It is evident however that these conclusions are not completely correct. Firstly, while the oxalate complex undergoes racemisation, the chiral inductor will also racemise. Moreover, in many cases equilibrium is established in the system more rapidly than racemisation of $[Co(ox)_3]^{3-}$ takes place even in the presence of the optically active [M(diamine)$_2$(X)(Y)], which is an indication that it is not racemisation that is the rate-determining stage for PE.

A whole series of studies by Japanese authors[122–133] is devoted to the effect of different factors (the ionic strength of the solution, the presence of the organic solvent, the type of optically active inductor) on the magnitude of PE. In several studies[125,126,134–138] data on the structure of the associates formed in solution are given. According to these data, various interactions — ionic, hydrophobic, van der Waals — can cause the formation of adducts.[131] Even when the same charges occur on a complex and inductor it does not exclude the possibility of their association.

In the majority of cases the formation of associates occurs through hydrogen bonding. This conclusion is supported by the results of studying the structure of associates by both indirect methods[125–127,139] and the direct findings of X-ray diffraction analysis.[140–143]

Bosnitch and Watts[144] calculated the thermodynamic parameters of the shift in chiral equilibrium for a $Ni(phen)_3$ complex in (−)-2,3-butanediol: $\Delta H = -119$ cal mol^{-1} and $\Delta S = -0.28$ cal K^{-1} mol^{-1}. They also determined the rate constants of racemisation of (+)- and (−)-$Ni(phen)_3$ in this solvent and detected a difference in the rates of racemisation of the enantiomers which was in good agreement with the magnitude of the shift of the chiral equilibrium in the system (+)-$Ni(phen)_3$ − (−)-2,3-butanediol.

Mayer[145] had previously reported some results for the system (+)-$Ni(phen)_3$ − *L*-Glu that were not in such good agreement; the time of half-racemisation of the complex in this system was 14 h

while the PE equilibrium was reached after only 25 min. In order to overcome this contradiction, Mayer[145] proposed a new mechanism for PE—the mechanism of asymmetric modulation. Gillard et al.[146] suggested that the possibility of hydration of the phenanthroline or dipyridyl ligands (it is complexes of these ligands which are most widely used for studying PE), which results in the formation of new asymmetric sites, should be taken into account.

These studies indicate that in a number of cases PE can include specific processes inherent in individual systems, but these processes should not be regarded as general principles of the PE mechanism, especially as all the contradictions mentioned above can readily be eliminated if the enantioselectivity of association is taken into account.

Barton et al.[147] explain the phenomenon of PE in deoxyribonucleic acid (DNA) with $[Zn(phen)_3]^{2+}$ from these points of view, while Bartery et al.[148] use the same explanation for the change in peroxidase activity of an enzyme in the presence of Fe^{3+} chelates. It was subsequently shown[149] that enantioselective association of DNA also takes place with the $[Ru(phen)_3]^{2+}$ complex, with the right-hand spiral of DNA containing mainly the Δ-isomer of the complex. Yamagishi[150] confirmed these observations in the case of other tris-chelate complexes of transition metals.

It is interesting to note that if a $[Ru(phen)_2Cl_2]$ complex is used instead of $[Ru(phen)_3]^{2+}$ and hence there is a change from outer-sphere complex formation to inner-sphere (Cl ions are replaced), the Λ-structure of $[Ru(phen)_2Cl_2]$ will mainly be contained in the DNA spiral,[151] with one $[Ru(phen)_2]^{2+}$ species for every 11 pairs of nucleic bases. Thus, the enantioselectivity of inner- and outer-sphere coordination in these very similar systems proved to be directly opposite. A review was published by Barton[152] on the studies of enantioselective coordination of DNA with transition metal complexes, and the mechanism of the interaction of DNA with ruthenium complexes is discussed in detail in another study.[153]

Hemmes and Lee[154] studied PE for a complex of $[Zn(phen)_3]^{2+}$ with adenosine monophosphate and related compounds. They found quite considerable optical activity brought into this system, and they related it to the formation of associates with the following composition: 1 molecule of $[Zn(phen)_3]^{2+}$ to 2 molecules of adenosine monophosphate. The strength of these associates is mainly achieved through electrostatic interactions.

Association processes have also been studied in a fairly detailed manner for kinetically inert complexes.[136,155–167] In a number of systems thermodynamic enantioselectivity has been reliably detected. Formation constants of associates were not determined for some complexes but it has been clearly established by indirect methods[168,169] that they differ. In other cases the difference between the constants is within the limits of experimental error or absent altogether,[170,171] and hence PE is solely due in this case to the difference in chiro-optical properties of the diastereomeric associates.

Attempts have been made over a long period of time to establish a correlation between the absolute configuration of a chiral compound and the sign of PE occurring for it.[106,121,172–176] Definite progress was made in this direction but, as is noted by Miyoshi et al.,[177] it is first of all necessary to make an accurate assignment of the transition in the circular dichroism spectrum on which the correlation is carried out, and this is not always possible. Moreover, the occurrence of PE is due to a whole number of processes, the relative importance of which can vary significantly from system to system. Moreover, the suggestion put forward by Kirschner and Ahmad[176] that the observed PE reflects the spectroscopic characteristics of that enantiomer of the complex with which the solution is enriched gives rise to doubt.

Brittain et al.[178–187] studied the induced optical activity of tris-complexes of Eu(III) and Tb(III) with pyridine-2,6-dicarboxylic acid or 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-diol in the presence of amino acids,[178,179] optically active chromium complexes,[180] amino alcohols,[181,182] ascorbic acid,[183] hydroxyphenyl derivatives of amino acids,[184] *N*-substituted amino acids,[185,186] and sugars.[187] Thus, the study of PE was extended to lanthanide complexes. The results obtained in these studies[178–187] are of considerable significance for the determination of the optical purity of organic compounds using a chiral shift reagent. In fact, in this case the formation of an outer-sphere complex (and perhaps an inner-sphere one) also takes place, and since an optically active lanthanide complex and a racemic (or enantiomerically enriched) organic ligand take part in reaction, the reaction can be enantioselective. Therefore the intensity of the signals from the two diastereomeric associates can depend, in addition to other factors, on the enantioselectivity of this process. Although NMR is extensively used to determine optical purity (see, for example, two studies[188,189] and subsequent reports[190–194]), its use for studying the enantioselectivity of complex formation has not been widely applied so far (see the study of Krasutskii et al.[195] and the references in it).

A very special case was reported in 1978 by Garvey and Pope.[196] The authors found PE in the heteropolyanions $[P_2Mo_{18}O_{62}]^{6-}$ and α-$[P_2W_{18}O_{62}]^{6-}$ in the presence of *l*-brucine. Another similar system—$[MnMo_9O_{32}]^{6-}$—was later found by Nomija et al.[197] Since the structure of a heteropolyanion rules out the possibility of its racemisation, PE occurs here solely as a result of the difference in the association constants and the differences in the chiro-optical properties of the adducts [equilibria (2) and (3) in the scheme given above do not occur].

In conclusion we should mention the study of Shigematsu et al.,[198] in which the formation of an axial adduct between a trifluoroacetyl-*d*-camphor copper(II) complex and phenylethylamine was studied. The formation constant of the adduct with the *d*-amine was approximately 2.5 times higher than with the *l*-amine. Formally this system can be classed as a complex with inner-sphere ligand exchange, since direct binding between the amine and the metal atom occurs in the adduct, and also as an outer-sphere complex, since the axial ligands are bonded to the copper atom much more weakly than the ligands of the main coordination sphere.

V. Enantioselective effects in the reactions of coordination compounds that occur without ligand exchange

A typical example of a potentially enantioselective reaction that takes place without involving a chiral chemical compound is the action of circularly polarised light on complexes (similar reactions are known for racemic organic compounds).[199] The essence of this effect is that enantiomers absorb light energy to a different degree when they are irradiated with right-handed and left-handed circularly polarised light.[200,201] This can lead to an unequal degree of photodestruction or other photochemical processes and hence to an accumulation in solution of that enantiomer which absorbs light energy to a lesser extent. Of course, for this effect to occur it is essential that racemisation of the complex without irradiation takes

place very slowly or not at all. Enantioselective photolysis was demonstrated experimentally in the case of complexes of Cr(III) with acetylacetone or its derivatives,[201–206] oxalic acid,[207,208] and phenanthroline,[209] in which the fundamental rate constant of racemisation has a value of the order of 10^{-6} s^{-1}. In all cases the observed enantiomeric enrichment did not exceed 5%, which is an indication of the small degree of enantioselectivity of such processes.

Approximately the same degree of enantiomeric enrichment also occurred in systems where linearly polarised light was used rather than circularly polarised light, but irradiation was carried out in an optically active medium.[209] The difference in the absorption of light in this case was due to the formation of diastereomeric associates. Yoneda et al.[210] studied these processes in greater detail in $[Cr(ox)_3]^{3-}$, $[Cr(ox)_2(phen)]^-$, $[Cr(ox)(phen)_2]^+$, and $[Cr(phen)_3]^{3+}$ complexes in the presence of *d*-cinchonine or *l*-cinchonidine. They established that a solution on irradiation is enriched with the same enantiomer of the complex which accumulates as a result of dark PE.

Less conclusive results were obtained by Norden[211] by irradiation of a solution of Cr(III) in the presence of racemic tartaric acid with circularly polarised light. In this solution a large number of isomeric forms of complexes can be formed and it is not clear towards which isomers the equilibrium is shifted on irradiation. Norden[211] suggests that the occurrence of optical activity in solution is mainly due to the isomerisation

$$\Lambda\text{-Cr}(R\text{-tart})_3 \rightarrow \Delta\text{-Cr}(R\text{-tart})_3$$
and
$$\Delta\text{-Cr}(S\text{-tart})_3 \rightarrow \Lambda\text{-Cr}(S\text{-tart})_3.$$

The question of enantioselectivity occurring in electron-transfer reactions between complexes also proved to be controversial. It was reported[212] that if the racemic complex $[Cr(phen)_3]^{2+}$ is oxidised by Λ-$(+)_D$-$[Co(phen)_3]^{3+}$, 92% Δ-$(-)_D$-$[Cr(phen)_3]^{3+}$ and 8% Λ-$(+)_D$-$[Cr(phen)_3]^{3+}$ is formed. However, Kane-Maguire et al.,[213] having checked these results, could not detect any noticeable optical activity in the resulting $[Cr(phen)_3]^{3+}$. She then studied a further 13 different systems in which electron transfer occurs and in which enantioselectivity could be expected to occur, but her endeavours were unsuccessful. She concluded from these results that enantioselectivity is not present in outer-sphere redox processes.

Geselowitz and Taube,[214] having examined the results of previous studies,[213] came to the conclusion that the required ratio of the rates of oxidation to racemisation was not fulfilled, so enantioselectivity could not be detected. Having chosen as their research topic the reaction between Δ,Λ-$[Co(edta)]^-$ and Δ-$[Os(bipy)_3]^{3+}$, they demonstrated that this reaction leads to the formation of $[Co(edta)]^-$ that is 3% enriched with the Δ-isomer. Similarly, when Λ-$[Os(bipy)_3]^{3+}$ was used, the same excess of Λ-$[Co(edta)]^-$ was obtained. Subsequently, these and a number of other electron-transfer reactions were studied in detail by Lappin et al.[215–219] They confirmed that enantioselectivity occurred in these processes and noted the important role of the conformation of the ligands[215] and the structure of the complex[219] for enantioselectivity to take place. They also showed that there was a correlation between the enantioselectivity for formation of outer-sphere associates between oxidising agent and reducing agent and the enantioselectivity of electron-transfer.[216,217] The important role of the solvent in these processes was studied by Geselowitz et al.[220]

In studying energy transfer (from emission spectra) between terbium and europium ions, Brittain[221] found that complexes of terbium with racemic aspartic acid transfer their energy to a europium ion more effectively than complexes with optically active aspartic acid. It is worthy of note that all attempts to find any difference in the properties of complexes of terbium with *R*- or *S*- and *R,S*-aspartic acids by other methods (potentiometric titration, spectrophotometry) were unsuccessful.

Enantioselectivity was shown to occur in processes involving electrochemical oxidation/reduction of complexes when this process is carried out using an optically active electrolyte. Thus, the reduction of $Co(acac)_3$ in the presence of trimethyl-(–)-menthylammonium results in optical activity in the unreduced complex.[222,223] The enantioselectivity of this process was small, but Ohkubo et al.[222,223] were confident of increasing it through the choice of a suitable supporting electrolyte.

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The photochemistry of azines

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ABSTRACT. The features of the luminescence spectra and photochemistry of heterocyclic amines, such as derivatives of pyridine, quinoline, acridine, and diazines, in liquid and solid solutions are examined. The relationship between the composition of the lowest electronically excited states and the luminescence and photochemical properties is analysed. Particular attention is given to the nature of the photochemically active, electronically excited state.

The bibliography includes 106 references.

Contents

I.	Introduction	164
II.	Features of the luminescence spectra	164
III.	Photochemical properties	170

I. Introduction

At the present time the theoretical treatment of the mechanisms of photolytic processes in complex organic molecules and the reactivity of excited states are based on the findings of photophysics obtained by studying the luminescence spectroscopic properties of these systems. Progress in the photophysics of complex molecules (the relationship between the spectroscopic properties and structure,[1–4] the effect of the medium, the theory of radiationless transfers[5–10]) has considerably outstripped the advances in theoretical photochemistry. This circumstance is to a considerable extent due to the absence of data on the multiplicity and nature of the orbitals of the photochemically active, electronically excited state; a very limited number of photochemical reactions have been characterised through a reliable value of the quantum yield. In the present review the data on the reactivity of six-membered azines have been correlated on the basis of theories on the fundamental photochemical processes.

II. Features of the luminescence spectra

1. Pyridine, quinoline, and isoquinoline

The composition of the lowest electronically excited states and luminescence properties of six-membered *N*-heterocyclic compounds have been examined in monographs.[5,9] These compounds, including pyridine, quinoline, isoquinoline, and acridine, differ formally from aromatic hydrocarbons in that they have an $-N=$ atom instead of a methylene group. In this case the π-system remains unchanged and the absorption spectra of such compounds have much in common with the spectra of the hydrocarbon analogues of *N*-heterocycles since in both cases they result to a considerable extent from $\pi \rightarrow \pi^*$ transitions. These $\pi \rightarrow \pi^*$ transitions have the same polarisation as the transitions that give rise to the absorption and fluoroscence spectra of aromatic hydrocarbons.[5]

In the absorption spectra of pyridine the $\pi \rightarrow \pi^*$ bands (λ_{max} = 255 and 195 nm, ε_{max} = 1800 and 7500 litres mol^{-1} cm^{-1}) are more intense than the corresponding bands for benzene. This is because the electronegative nitrogen atom disturbs the symmetry of the π orbitals, so that while there is a complete similarity of the $\pi \rightarrow \pi^*$ transitions in benzene and pyridine the latter are more probable[6] (Table 1).

Table 1. Spectroscopic properties of azines.[15,16]

Compound	Molecular symmetry	Energy of $S(\pi, \pi^*)$ state, eV	Energy of $S(n, \pi^*)$ state, eV	φ_{ISC}	φ_f
Pyridine	C_{2v}	4.75	4.27	—	6×10^{-5} [a]
Quinoline	D_{2h}'	3.97	3.6	0.31[b]	—
"	—	—	—	0.50[c]	
"	—	—	—	0.065[d]	—
Isoquinoline	D_{2h}'	3.92	3.6	0.24[c]	—
2,2'-Dipyridyl	—	—	—	—	5×10^{-3} [d]
"	—	—	—	—	9×10^{-3} [d]
Pyridazine[e]	C_{2v}	4.90	3.30	—	—
Pyrimidine[e]	C_{2v}	5.00	3.85	—	—
Pyrazine	D_{2h}	4.64	3.83	—	—
S-Triazine	D_{3h}	5.45	3.84	—	—
S-Tetrazine	D_{2h}	2.41	2.23	—	—
1,2,4-Triazine	D_{2h}'	—	2.75	—	—
Quinoxaline	C_{2v}	3.84	3.30	—	—
Cinnoline	C_s	3.84	3.30	—	—
Phthalazine[e]	C_{2v}	4.09	3.20	—	—
Acridine[e]	C_{2v}	3.30	3.30	—	—
Phenazine[e]	D_{2h}	3.25	2.85	–	—

Note. φ_{ISC} and φ_f are the quantum yields for intersystem crossing and fluorescence; [a] gas, normal conditions; [b] in benzene; [c] in a butanol : isopentane (3 : 7) mixture at 77 K; [d] in hexane; [e] the luminescence properties are given in more detail in Table 10; unmarked values are given for solutions in cyclohexane.

By studying the electronic spectra of pyridine, pyrazine, and pyrimidine in compressed gases and comparing the π-electron systems of heterocycles and benzene it was possible to deduce that the π-electron systems of pyridine in the $^1B_{2u}$ and $^1B_{1u}$ π,π*-states

(notation adopted by analogy with benzene) and also those of pyrazine and pyrimidine in the $^1B_{1u}$ state resemble the corresponding system in benzene. In the transition of diazines to an excited $^1B_{2u}$ state, their π-electron systems are considerably different from that of benzene.[11–13] At the same time the excitation of pyridine, which is accompanied by the appearance of a band due to a $^1B_{1u}$ transition, is considerably different from the analogous excitation of benzene (the ^1B band of benzene corresponds to the transition to a $^1E_{1u}$ state, so comparisons cannot be made between these molecules in this excited state). In addition, pyrazine completely resembles benzene in its excitation to a $^1B_{2u}$ state.[14]

Apart from π,π* bands, in the spectra of pyridine and quinoline derivatives there are bands due to $n \rightarrow \pi^*$ transitions, which are directed perpendicular to the plane of the molecule. The occurrence of these transitions only slightly alters the absorption spectra of the molecules but has a very marked effect on the luminescence properties, which differ considerably from the properties of their hydrocarbon analogues.[5]

Zelikina et al.[14] were the first to record directly structural n,π^* bands in the spectra of solutions of pyridine, pyrazine, and pyrimidine in compressed krypton, xenon, and CF_4 (120–200 K). In the case of pyridine the $n \rightarrow \pi^*$ is superimposed on the long-wavelength section of a more intense $\pi \rightarrow \pi^*$ band. The vibronic structure of the n,π^*-band is completely eliminated even in hexane at room temperature,[14] i.e., intramolecular interactions can only be minimised in compressed gases. All these n,π^* bands undergo a bathochromic shift when there is a change from rarefied vapour to solutions in Kr and He.[14–17]

The luminescence properties of azines are determined by the relative configuration of the lowest electronically excited states of n,π- and π,π^*-type (Fig. 1). Heterocycles luminesce very weakly, whereas the corresponding aromatic hydrocarbons exhibit marked fluorescence and phosphorescence.[5] Pyridine hardly fluoresces at all and does not phosphoresce, quinoline does not fluoresce in non-polar solvents but fluoresces in polar solvents (π,π^*-type fluorescence), while acridine exhibits weak fluorescence in all aliphatic solvents but in alcohols the fluorescence increases markedly (see Table 2). Only for quinoline and isoquinoline has π,π^*-type phosphorescence been recorded.

In one monograph[5] the features of the luminescence spectra of monoazines are examined in a somewhat simplified manner, only in relation to the structure and relative configuration of the lowest electronically excited states and without taking into account the interaction between them, even though this interaction has a decisive effect on radiationless deactivation processes.[9] Thus, it is assumed that for all monoazines $T(\pi,\pi^*)$ is the lowest state and in this case only π,π^*-phosphorescence can occur. As the size of the π-system increases, the energy of the $S(\pi,\pi^*)$ state decreases more rapidly than that of $S(n,\pi^*)$, so that even in quinoline in the vapour phase and in hydrocarbon solvents the energies of the $S(\pi,\pi^*)$ and $S(n,\pi^*)$ states coincide. In all these amines with a single nitrogen atom (apart from pyridine) the n,π^* band is not at longer wavelength, and *N*-heterocycles in which the π,π^* band in the absorption spectrum occurs at shorter wavelength than in acridine must exhibit π,π^*-phosphorescence (Fig. 1).

In acid media and polar solvents (especially when intramolecular hydrogen bonds are formed with the nitrogen atom of the heterocycle), those molecules in which the energy of the $T(n,\pi^*)$ state is higher than that of the $S(\pi,\pi^*)$ states (quinoline, azaphenanthrene, acridine, and benzacridine)[5] start to fluoresce (Table 2).

The fluorescence of pyridine, quinoline, isoquinoline, and acridine is exceptionally weak or absent altogether in aprotic solvents but quite considerable in protic solvents,[9,15] and it is assumed that even this weak fluorescence in aprotic solvents is due to impurities.[9] However, the decrease in quantum yield of fluorescence in aprotic solvents is not due to an increase in intersystem crossing; for

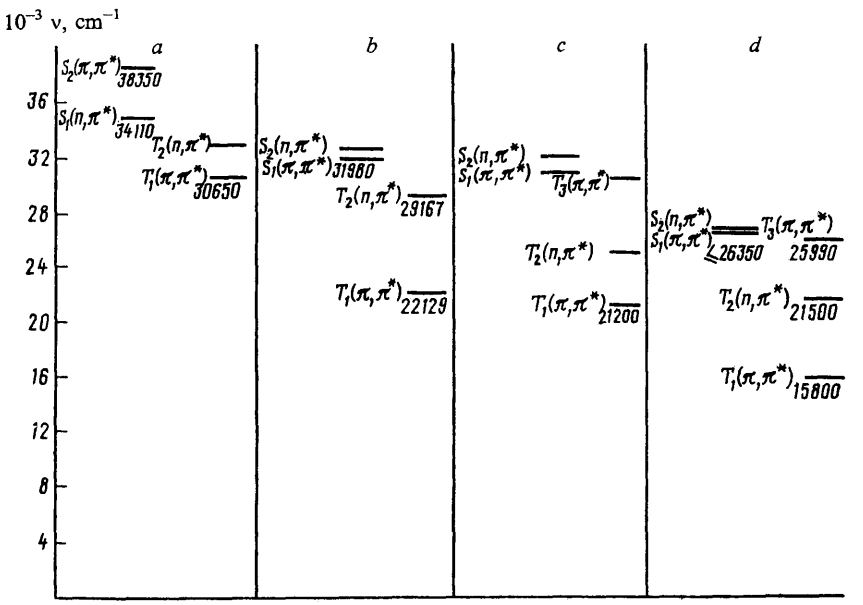


Figure 1. Distribution of the lowest energy levels of monoazines in non-polar solvents:[18–20] *a*, pyridine; *b*, quinoline; *c*, isoquinoline; *d*, acridine.

quinoline and isoquinoline the yields in the triplet state are equal to ~0.2 and 0.3 respectively.[9] Therefore the absence of fluorescence in these compounds in aprotic solvents is related to an acceleration of the $S_1 \rightarrow S_0$ internal conversion. This increase in internal conversion is due to a vibrational interaction between the closely situated $S(n,\pi^*)$ and $S(\pi,\pi^*)$ levels or, particularly in the case of quinoline and isoquinoline, to a perturbation (or even conversion) of the state as a result of movement along the coordinate corresponding to an extraplanar "scissor" vibration (in other words, as a result of a Jahn–Teller pseudoeffect). This perturbation (or inversion) must lead to a considerable increase not only in the rate of $S_1 \rightarrow S_0$ conversion but also $S_1 \rightarrow T_1$ intersystem crossing (experimentally this is exhibited by the lack of dependence of the quantum yield in the triplet states of quinoline and isoquinoline on the solvent[9]).

Thus, a vibrational interaction between the singlet n,π^* and π,π^* states of virtually all monoazines results in an extremely rapid radiationless deactivation of the S_1 state. The rate of radiationless deactivation in the gas phase increases sharply on excitation of the extraplanar scissor vibration of the lowest excited state.[26,27]

The main contribution to internal conversion of the thermalised S_1 state is provided by the highest vibrational sublevels of the S_1 state. In a deuteriated compound this effect is even more important since the frequency of the scissor vibration decreases, resulting in a reverse isotope effect in internal conversion.

On going from aprotic solvents to protic ones the π,π^* bands undergo a bathochromic shift while the n,π^* bands experience a hypsochromic shift. Consequently, if the lowest singlet state in the heterocyclic amine is a π,π^* state [or if the $S_1(n,\pi^*)$ levels are situated only just below it], the increase in the distance between the S_1 and S_2 levels results in a sharp decrease in the rate of internal conversion.[28]

Confirmation of the decisive role of a vibrational interaction between the n,π^* and π,π^* states in the luminescence of monazines (the "proximity effect")[9] is provided by the temperature dependence of the quantum yield of fluorescence. The quantum yield of fluorescence for isoquinoline in ethanol decreases markedly with an increase in temperature.[9,29] In this case the quantum yield of intersystem crossing (ISC) is virtually independent of temperature (~0.2 and ~0.3 at 298 and 77 K respectively). As the temperature increases the hydrogen bonds between isoquinoline and ethanol are weakened, resulting in a convergence of the $S(\pi,\pi^*)$ and $S(n,\pi^*)$ states and an intensification of the vibrational interaction, i.e., on heating the rates of $S_1 \rightarrow S_0$ and $S_1 \rightarrow T_1$ conversions increase simultaneously. As we shall see below, the "proximity effect" in one form or another determines the luminescence properties of all aromatic azines.

The kinetics of the decay of the triplet state of pyridine in the vapour phase are non-exponential. This is due to the existence of two closely situated triplet states that have different lifetimes. A model has been put forward in which it is assumed that there is a strong vibrational interaction between the almost degenerate $T(\pi,\pi^*)$ and $T(n,\pi^*)$ states of pyridine, which results in the appearance of a double minimum on the potential surface of the T_1 state[30,31] in the direction of the extraplanar "scissor" vibration. In this case the thermally relaxed T_2 state of pyridine is non-planar while the activated state is planar, and the rate constants for $T_1 \rightarrow S_0$ relaxation of these two states differ, amounting to less than 10^5 and 5×10^6 s^{-1} respectively.

A study of the hyperfine splitting at zero field of pyridine and its derivatives[32] has confirmed that the $T_1 \rightarrow S_0$ transition in pyridine is forbidden (this is evident from the small intensity of the O–O band). The occurrence of this transition is due to a vibrational interaction of the lowest triplet state with the closest $^3E(\pi,\pi^*)$ state and its spin-orbit interaction with $\sigma\pi^*$ and $\pi\sigma^*$ singlet states. In neutral molecules the vibrational interaction of the singlet $S(\pi,\pi^*)$ states with $T(n,\pi^*)$ states is apparently not strong enough to affect

Table 2. Luminescence spectral and photochemical properties of acridine and its derivatives.

Compound	Solvent	φ_{fl}	φ_{ISC}	τ_{fl}, ns	E_a, kJ mol^{-1}	φ_m^S	φ_{rad}^S	φ_m^T	φ_{rad}^T	φ_{tot}	Refs.
Acridine	Ethanol	0.09	—	—	16.0	0.043	0.043	0	0.043	0.129	[18, 19]
Acridine	Methanol	0.09	—	—	18.2	0.027	0.032	0.006	0.063	0.128	[18]
Acridine	Benzene	0.00061	0	—	4.1	—	—	—	—	—	[18, 20]
Acridine	Isopropanol	0.12	—	—	14.0	0.03	0.058	0	0	0.088	[18, 20–22]
Acridine	Toluene	0.001	0.05	—	—	—	—	—	—	0.05	[23]
Acridine	t-Butanol	—	0.61	—	—	—	—	—	—	0.01	[22]
Acridine	Anisole	0.07	—	—	—	—	—	—	—	0.01	[22, 24]
Acridine	Acetonitrile	0.03	0.42	2.1	6.7	—	—	—	—	0.02	[16, 21]
Acridine	n-Hexane	0.0005	0.5	—	4.0	—	—	—	—	—	[17, 21]
Acridine	Water/KOH (pH 12)	0.37	0.5	11.0	22.7	—	—	—	—	—	[25]
Perdeuteroacridine	Water/KOH (pH 12)	0.31	—	11.5	—	—	—	—	—	—	[25]
9-Chloroacridine	Water/KOH (pH 12)	0.26	—	6.5	—	—	—	—	—	—	[25]
9-Methylacridine	Water/KOH (pH 12)	0.38	—	9.5	—	—	—	—	—	—	[25]
9-Propylacridine	Water/KOH (pH 12)	0.43	—	10.4	—	—	—	—	—	—	[25, 26]
9-Aminoacridine	Water/KOH (pH 12)	0.81	—	15.4	—	—	—	—	—	—	[27]
9-Methyl-3,4-benzo-acridine	Toluene	0.08	—	3.0	—	—	—	—	—	—	[25]
1,2,7,8-Dibenzo-acridine	Toluene	0.22	—	8.0	—	—	—	—	—	—	[28]
1,2,3,4,5,6,7,8-Tetra-benzoacridine	Toluene	0.24	—	12.0	—	—	—	—	—	—	[28]

Note. τ_{fl} is the lifetime of fluorescence; E_a is the energy of activation obtained from the temperature dependence of φ_{fl}; φ_m^S, φ_{rad}^S, φ_m^T, and φ_{rad}^T are the quantum yields for photoreduction of acridine from singlet and triplet states by a molecular and radical mechanism respectively.

the vibrational structure of the hyperfine splitting parameters at zero field. Phosphorescence of the pyridinium cation occurs from the $^3A_1(\pi,\pi^*)$ state (originating from "removal" of the n,π states) and has much in common with the phosphorescence of benzene. Thus, although the symmetry of pyridinium (C_{2v}) is lower than the symmetry of benzene, replacement of carbon by nitrogen leads to only a slight perturbation of the spin-orbit interaction in the benzene ring.

2. Acridine

The pattern of distribution for the lowest electronically excited states of acridine has been quite reliably established (Fig. 2). Previously the dependence of the quantum yield of the fluorescence of acridine on the solvent was interpreted as the result of a change in the nature of the S_1 state—π,π^* in protic solvents and n,π^* in aprotic solvents.[28,33] The lifetime of the S_1 state of acridine is equal to 50 ± 6 ps in hexane and 350 ps in ethanol.[34] However, after the detection of acridine fluorescence in a matrix of n-octane at 77 K and in benzene at room temperature,[35] it was accurately established that even in these solvents the lowest level corresponds to the $S_1(\pi,\pi^*)$ state.

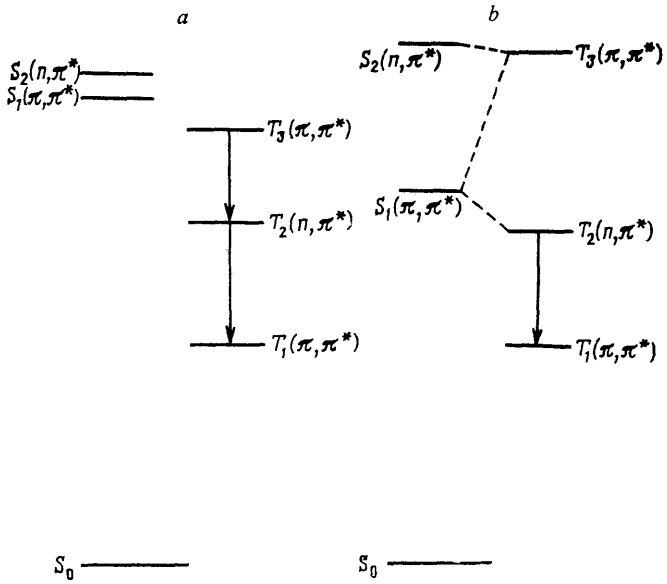


Figure 2. Distribution of the lowest energy levels of the electronically excited states of acridine: *a*, in benzene; *b*, in water at pH > 7.

Acridine undergoes photoreduction in solvents that can readily eliminate a hydrogen atom, and its lowest electronically excited state varies in different solvents (Fig. 2).[17] It was found that the φ_{ISC} of acridine decreases as the temperature increases in reactive solvents (methyl methacrylate and polymethyl methacrylate) and does not depend on the temperature in benzene (in which there is no photoreduction). In the opinion of Kasama and Kikuchi,[17] in water ISC takes place from the $S_2(n,\pi^*)$ state, which is thermally populated as a result of the following sequence of processes: $S_1(\pi,\pi^*) \rightleftarrows (\Delta E)S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$ (ΔE is the difference in energy between the S_1 and S_2 states). In benzene ΔE is very small and ISC takes place very rapidly, while in water ΔE = 1900 cm^{-1} and internal conversion can thus compete with ISC.[36] Schmidt et al.[36] determined the values of ΔE for acridine in different solvents; but it was mistakenly assumed by them that the lowest state of acridine is the $S_1(n,\pi^*)$ state (see Table 2).[37]

The fact that the sum of φ_R + φ_{ISC} + φ_{PR}† for acridine in solvents that are capable of eliminating a hydrogen atom is less than the sum of φ_R + φ_{ISC} in inert solvents, suggests that acridine is deactivated by removal of hydrogen and subsequent recombination.

In the radiationaless deactivation of the S_1 state of acridine an important role is played by the $T_3(\pi,\pi^*)$ state,[32] whose energy is equal to 26050 cm^{-1} in all solvents[38] and does not depend on the polarity of the latter.[17,37]

The magnitude of the energy gap between the electronically excited state of acridine depends also on the presence of substituents in the molecule and the annelation of the benzene rings (Table 2).[17] In all the acridine derivatives there are two routes for ISC to occur, with the rate of the process in one of them dependent on temperature and in the other not dependent on temperature. For all the acridines (except for 9-aminoacridine) the rate of the process: $S_1(\pi,\pi^*) \rightleftarrows (\Delta E)S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ is dependent on temperature and the process: $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$ is independent of temperature.[39]

In the case of 9-aminoacridine the energy gap is large, $\Delta E(T_3-S_1)$ = 4360 cm^{-1}, so participation of the T_3 state in the deactivation of the $S_1(\pi,\pi^*)$ state can be ignored (Table 2). The electron-donating NH_2 group gives rise to a hypsochromic shift of the n,π^* bands and a bathochromic shift of the π,π^* bands in the absorption spectrum, so the $T_2(n,\pi^*)$ level of 9-aminoacridine is higher than $S_1(\pi,\pi^*)$ and the dependence on temperature is solely determined by the possible transition $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$.

Up to the present time there is still much that is unclear in the photophysics of acridine. Thus, the energy of activation of the fluorescence process of acridine in hexane and ethanol does not depend on the nature of the solvent, which cannot be explained by limiting the study to just the "proximity effect."[42]

3. Diazines

The lowest excited states of pyrazine, pyrimidine, and pyridazine are of an n,π^*-type.[5] The gas-phase absorption spectra exhibit a well resolved vibrational structure in the region of the n,π^* transition (Fig. 3).

The lowest T_1 state of pyrazine and pyrimidine is the $T_1(n,\pi^*)$ state. When methyl substituents are introduced in the molecule, the $T(\pi,\pi^*)$ band experiences a bathochromic shift but the $T(n,\pi^*)$ band undergoes a hypsochromic shift, so the $T(\pi,\pi^*)-T(n,\pi^*)$ energy gap in methylated diazines is much less than in the initial unsubstituted compounds.[9] As the width of the gap decreases the quantum yield and lifetime of n,π^*-phosphorescence decrease considerably.[9] The change in the value of φ_R for these compounds on methylation is solely due to the increase in probability of the radiationless transition $T_1(n,\pi^*) \rightarrow S_0$ (Table 3).

The dependence of the quantum yield of fluorescence on the excitation energy for pyrazine and pyrimidine vapour (Figs. 4 and 5) suggests[39] that while the rate constant k_{ISC} in the region of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ absorption bands is constant, the rate

† φ_R is the quantum yield of photoreduction.[40,41]

constant for internal conversion k_{IC} ($S_1 \rightarrow S_0$) increases sharply (to 10^{11} s^{-1}) for light with energy above 34 000 cm^{-1}. Thus, in the case of pyrazine, as for pyridine, at frequencies above 34 000 cm^{-1} a route for rapid radiationless deactivation occurs (having the same origins).

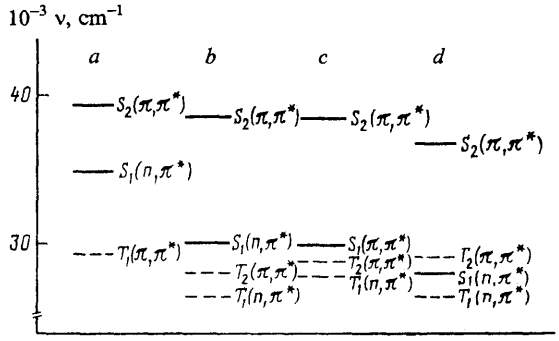


Figure 3. Distribution of the lowest energy levels of diazines: *a*, pyridine; *b*, pyrazine; *c*, pyrimidine; *d*, pyridazine.

Table 3. Quantum yields for intersystem crossing, fluorescence, and radiationless deactivation in the gas phase at a pressure of 1.0 mm Hg azine + 100 mmHg SF_6 (from the results of Yamazaki et al.).[38,40]

Compound	Transition	ν_{0-0}, cm^{-1}	φ_{fl}	φ_{ISC}	$k_{IC} \times 10^{-11}$, s^{-1}
Pyridine	$S_1(n,\pi^*) \leftarrow S_0$	34 769	$5.9 \cdot 10^{-5}$	0.30	0.17
	$S_2(\pi,\pi^*) \leftarrow S_0$	38 350	$2.4 \cdot 10^{-6}$	0.0067	7.68
Pyrazine	$S_1(n,\pi^*) \leftarrow S_0$	30 875	$1.3 \cdot 10^{-3}$	1.0	0.001
	$S_2(\pi,\pi^*) \leftarrow S_0$	37 840	$0.9 \cdot 10^{-4}$	0.13	5.25
Pyrimidine	$S_1(n,\pi^*) \leftarrow S_0$	31 072	$15 \cdot 10^{-3}$	1.0	0.001
	$S_2(\pi,\pi^*) \leftarrow S_0$	40 310	$0.4 \cdot 10^{-4}$	0.08	2.63

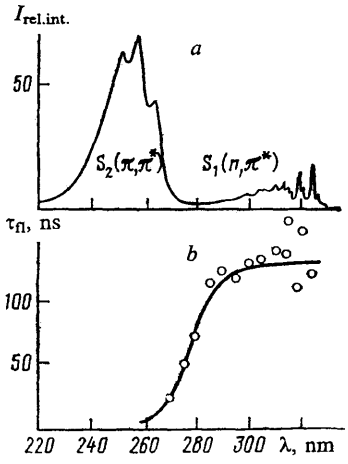


Figure 4. Absorption spectrum of pyrazine (*a*) and dependence of the lifetime of fluorescence (*b*) on the wavelength of excitation at a pyrazine pressure of 1 mmHg in the presence of SF_6.[39,40]

In contrast to pyrazine, k_{ISC} for pyrimidine increases with an increase in excitation energy near the S_1 band, which leads to an even more marked decrease in τ_{fl} and φ_{fl} (Figs. 4 and 5). The mechanism of this type of deactivation is possibly due to the acceleration of internal conversion as a result of photoisomerisation[43] (a similar mechanism has been proposed for benzene).

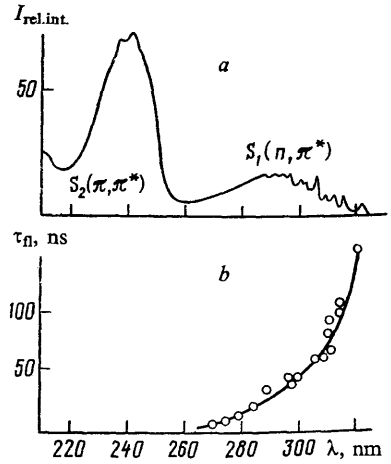


Figure 5. Absorption spectrum of pyrimidine (*a*) and dependence of the lifetime of fluorescence (*b*) on the wavelength of excitation[39,40].

The T_1 state of pyridine has been identified from the results of energy transfer studies;[44-47] only subsequently was the phosphorescence of pyridine itself detected.[44,45] The energy of this state has been estimated as 30 650 ± 800 cm^{-1},[48] and the lifetime for phosphorescence of pyridine vapour is several microseconds. The phosphorescence of pyridine derivatives—lutidines, cyanopyridines, and aminopyridines—in a condensed state is discussed by Motten and Kwiram.[32,49]

4. Phenazine

Phenazine may be regarded as pyrazine with annelated benzene rings. The absorption and emission spectra of phenazine have been studied in detail in solution and monocrystals at 77 and 4.2 K.[10,50] The relative configuration of the lowest electronically excited states $S_1(n,\pi^*)$, $S_2(\pi,\pi^*)$, and $T_1(\pi,\pi^*)$ has been established (Fig. 6).[51-53]

Fluorescence occurs for phenazine itself. It is of π,π^*-type in alcohols and n,π^*-type in hexane (Tables 4 and 5).

Struve et al.[42] used picosecond laser photolysis to record the $T-T$ absorption spectrum of phenazine in isooctane and methanol and demonstrate the existence of two different routes for population of the lowest $T_1(\pi,\pi^*)$ state of phenazine by excitation of the singlet $S_3(^1L_b)$ state: $S_3 \rightarrow S(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$ and $S_3 \rightarrow T_2(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$.

The introduction of F and Cl atoms into the β-position of phenazine leads to a successive increase in quantum yield of fluorescence. A subsequent change to Br and I reduces φ_{fl}, with a bathochromic shift of the fluorescence spectrum occurring. When a halogen is introduced into the α-position there is no fluorescence flashing and the fluorescence spectrum does not change (Table 4).[41]

In the opinion of Osipov et al.[52] πp_z-conjugation between the π-electron system and the halogen can result in this type of bathochromic shift of the π,π*-levels, so that inversion of the π,π* and lowest n,π^* level occurs. In the series F, Cl, Br, I the conditions for conjugation deteriorate since the 2-, 3-, 4- and 5-p_z electrons are involved.

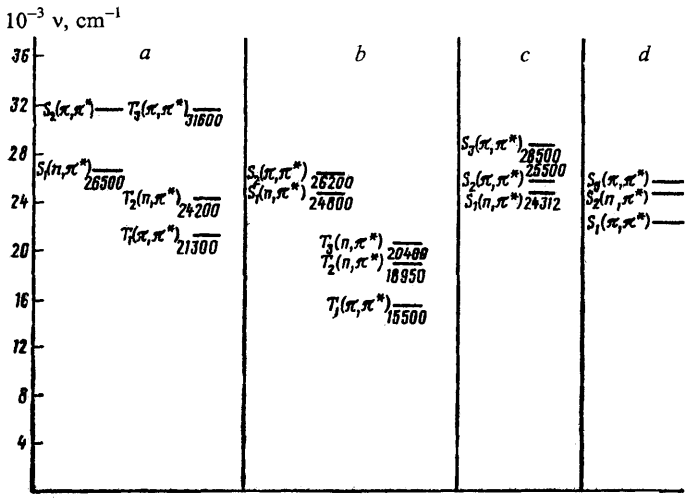


Figure 6. Distribution of the lowest energy levels of "anomalous" diazines.[92,96]

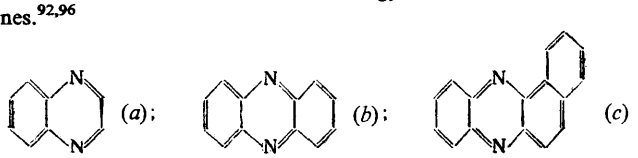


Table 4. Luminescence properties of phenazine derivatives in toluene at 20 °C.[41]

Compound	φ_n	τ_n, ns
Phenazine	$7\cdot10^{-4}$	0.06
1,2-Benzphenazine	0.012	0.2
1,2,3,4-Dibenzphenazine	0.10	0.18
1,2,3,4,5,6,7,8-Tetrabenzphenazine	0.16	1
1-Fluorophenazine	—	<2
1-Chlorophenazine	—	<2
2-Fluorophenazine	—	2
2-Chlorophenazine	—	3.5
2-Bromophenazine	—	5
2-Iodophenazine	—	5

An unusual effect involving the increase in quantum yield and lifetime of fluorescence of phenazine itself has been detected when toluene is replaced by methyl iodide as the solvent at 77 K.[52] This is apparently due to the formation of weak charge-transfer complexes between phenazine and methyl iodide in which the *n*-electrons of phenazine are partially bonded.

Annelation of the benzene rings causes a reduction in energy of the $S_2(\pi,\pi^*)$ state of phenazine, which leads to an increase in quantum yield and lifetime of fluorescence (Table 4). In this case inversion of the $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ levels does not occur, namely, for all the phenazines the $S_1(n,\pi^*)$ state is the lowest. However, the proximity of these levels suggests that there is a considerable temperature-dependent vibrational interaction between them. The temperature causes excitation of the vibrations linking the closely situated states and thus determining the features of the luminescence spectra of the molecules. Osipov et al.[41] attribute the two-component fluorescence of benzphenazine and dibenzphenazine to emission from the $S_2(\pi,\pi^*)$ and $S_1(n,\pi^*)$ states, i.e., for these molecules emission from the $S_2(\pi,\pi^*)$ state is more effective than from $S_1(n,\pi^*)$. Phenazine becomes a stronger base in its S_1 and T_1 states than in the ground state. Its mono- and di-protonated forms have been recorded (Table 5, see also Table 10 for comparison).

Table 5. Luminescence properties of phenazine (A), its monocation (AH^+), and dication (AH_2^{2+}).[53]

Compound	λ_{max}	λ_{0-0}	E_{T_1}, cm⁻¹	pK_{S_0}	pK_{T_1}	pK_{S_1}
A	21 000	23 500	15 475	1.24	4.0	6.0
AH^+	19 000	21 250	14 175	1.21	4.0	6.0
AH_2^{2+}	15 200	17 300	9 300	−4.30	5.7	4.1

Note. pK_{S_0}, pK_{S_1}, pK_{T_1} are the p*K* values in the ground, S_1 and T_1 states.

5. Aminopyridines

A class of pyridine derivatives such as aminopyridines has been studied in detail as have 7-azaindolines, which are very similar to them in structure.[54–63] A study of the features of the luminescence spectra and quantum-chemical calculations of the composition of the lowest electronically excited states of aminopyridines[55–58] showed that the amino group does not significantly perturb the energy levels of pyridine (Fig. 7). As in the case of pyridines, the features of the luminescence spectra of aminopyridine are determined to a considerable extent by the vibrational interaction between closely lying singlet n,π^* and π,π^* levels.[64,65] The effect of the amino group is to cause the distance between the lowest $S(n,\pi^*)$ and $S(\pi,\pi^*)$ levels to become even smaller, and in non-polar solvents inversion even occurs so that $S_1(\pi,\pi^*)$ becomes the lowest level.

According to calculations,[66] the $S_1(n,\pi^*)$ level of 2-aminopyridines is situated 0.72 eV below the $S_2(\pi,\pi^*)$ level. However, an analysis of the effect of the solvent on the luminescence properties of 2-aminopyridine and also a study of the vibrational and rotational structure of its spectra[57] show that even in non-polar solvents the lowest state is the excited $S_1(\pi,\pi^*)$ state, and the band at 298.0 nm corresponds to the $^1A_1 \leftarrow {}^1B_2$ transition in pyridine somewhat shifted by the effect of the amino group.

In non-polar solvents the distance between the levels increases and the efficiency of radiationless deactivation decreases, resulting in an increase in the yield of fluorescence, and there is a correlation between the strength of the oscillator of the $\pi \rightarrow \pi^*$ band and the quantum yield of fluorescence[55] (Table 6).

2-, 3-, and 4-Aminopyridines do not phosphoresce in non-polar solvents but phosphorescence occurs in polar solvents. According to Wolleben and Testa[57] this phenomenon is due to the increase in the rate of $S_1 \rightarrow T_1$ intersystem crossing, since in polar solvents the relative position of the $T(n,\pi^*)$ and $T(\pi,\pi^*)$ levels changes (Fig. 8).

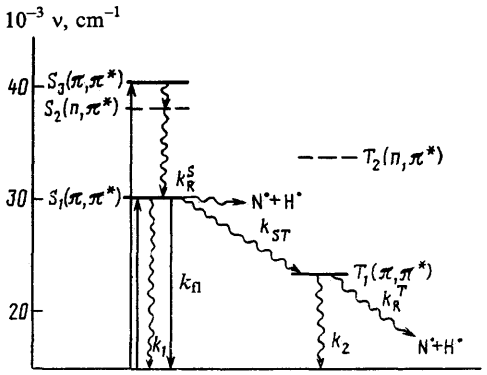


Figure 7. Distribution of the lowest energy levels of 5-methyl-7-azaindoline and rate constants for the fundamental processes taking place in it from the results of Dvornikov et al.:[59-62] $k_1 = 1.2 \times 10^8\ s^{-1}$; $k_2 = 2 \times 10^5\ s^{-1}$; $k_R^T = 8 \times 10^5\ s^{-1}$; $k_{fl} = 4 \times 10^7\ s^{-1}$; $k_{ISC} = 8 \times 10^7\ s^{-1}$; $k_R^S < 5 \times 10^6\ s^{-1}$; k_R^S and k_R^T are the rate constants of dissociation from the lowest singlet and triplet states respectively.

Table 6. Features of the luminescence spectra of 7-azaindolines and 2-aminopyridine.[55,57,59,60]

Compound	Solvent	λ_{abs}^{max}, nm	ε, $m^2 mol^{-1}$	λ_{fl}^{max}, nm	φ_{fl}	τ_0, ns	$k_{fl} \times 10^{-7}$, s^{-1}
2-Aminopyridine	Heptane	290	4250	332	0.04	24.2	6.2
5-Methyl-7-azaindoline	"	303	4610	350	0.17	3.9	7.3
4,6-Dimethyl-7-azaindoline	"	308	7340	360	0.18	2.2	9.1
4,6-Dichloro-7-azaindoline	"	308	6520	360	0.023	0.8	7.6
5-Methyl-7-azaindoline	Heptane + CH_3COOH	317	—	450	0.046	—	—
2-Aminopyridine	Propanol	296	4400	352	0.18	5.1	—
5-Methyl-7-azaindoline	"	308	4610	375	0.32	4.6	5.6
4,6-Dimethyl-7-azaindoline	"	310	7780	375	0.25	3.7	9.1
4,6-Dichloro-7-azaindoline	"	315	6790	385	0.0065	—	11.0
2-Aminopyridine	Acetonitrile	293	4800	345	0.45	5.0	—
5-Methyl-7-azaindoline	"	305	—	368	0.23	—	—
4,6-Dimethyl-7-azaindoline	"	310	—	368	0.21	—	—
4,6-Dichloro-7-azaindoline	"	312	—	370	0.0014	—	—

The relative position of the lowest n,π^* and π,π^* levels of 2-aminopyridine is highly dependent on the presence and nature of the substituent in the aromatic ring. The introduction of a methyl group into 2-aminopyridine (for example, the formation of 3-methyl-2-aminopyridine) leads to inversion of the lowest singlet n,π^* and π,π^* levels and to a reduction in width of the energy gap between them. Therefore the fluorescence of 3-methyl-2-aminopyridine occurs in non-polar solvents with the participation of the almost degenerate $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ states. At 77 K there is emission from S_2 while at room temperature it occurs from both states. The quantum yield of fluorescence is determined to a considerable extent by the strength of the oscillator of the long-wavelength π,π^* transition, with which the n,π^* transition is combined.[66] Calculations using the CNDO method showed[56] that as soon as the $S_1(\pi,\pi^*)$ state becomes the lowest state for 2-aminopyridine derivatives, this immediately leads to an increase in quantum yields of fluorescence in non-polar solvents. (Fig. 8).[67]

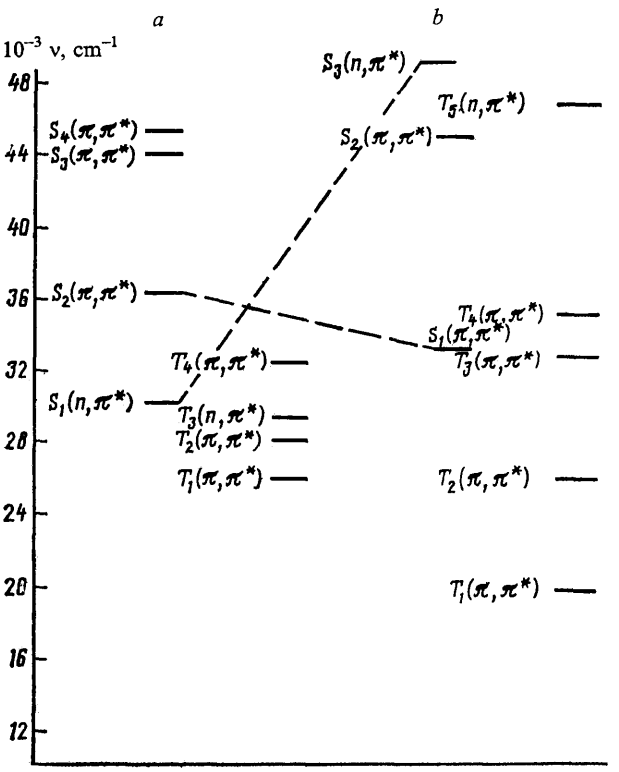


Figure 8. Distribution of the lowest energy levels of 2-aminopyridine (*a*) and its cation (protonated on the pyridine ring) (*b*).

III. Photochemical properties

1. Pyridine, quinoline, acridine

As already mentioned above, pyridine is isoelectronic with benzene, but in pyridine there is a system of nitrogen n,π^* states which does not occur in aromatic compounds. Hence the photochemical reactions of pyridine can be divided into those which are similar to the photochemical conversions of benzene and those which are determined by the presence of the unshared electron pair of nitrogen.

Amongst processes of the first type are photoisomerisation (formation of benzvalene, Dewar pyridine), photosubstitution, and also photodissociation of halide-substituted pyridines. Processes of the second type are represented by hydrogen abstraction reactions

(photoreduction), processes related to the acid-base dissociation of pyridines in an excited state, and processes involving cleavage of ring bonds.

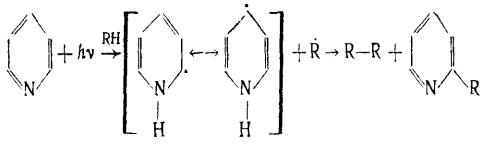
In the case of pyridine the photolytic processes that are typical of nitrogen-containing compounds occur via n,π^* excited states (as a rule the lowest in energy), while "benzene-type" reactions require excitation of the π-system.

a) Acid-base properties of pyridine. According to CNDO calculations, the basicity of heterocyclic aromatic compounds in which the heteroatom is the basic site is considerably higher in the S_1 state that in the S_0 state.[62] The basicity of pyridine derivatives in the S_1 state is in fact higher than that in the S_0 state by a factor of 3–4, but the basicity of quinolines increases less (Table 7). Moreover, in protonation of the pyridine ring there is a marked increase in energy of the n,π^* transitions compared to the π,π^* transitions, since the proton interacts with the unshared electron pair on nitrogen. According to calculations,[56] when 2-aminopyridine is protonated the energy of the $S_1(n,\pi^*)$ state increases by 2.51 eV, as a result of which the vibrational interaction between the $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ states disappears and there is a sharp increase in the quantum yield of fluorescence in the cations. The increase in the basicity of bromine-substituted pyridine on going from the ground state to the S_1 and T_1 states is more related to the strong electron-donating properties of bromine as a result of the stronger conjugation of the p,π orbital of bromine with the π orbital of pyridine in these states[62] (Table 7).

Table 7. Acid-base properties of derivatives of pyridine and quinoline in aqueous and aqueous alcohol solutions.[62–64]

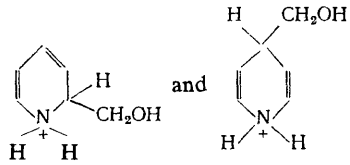
Compound	λ_{max}, cm^{-1}	pK_{S_0}	pK_{S_1}	pK_{T_1}
Pyridine	38 200	5.42	4.79	—
2-Bromopyridine	37 800	—	2.66	—
3-Bromopyridine	37 450	3.0	4.72	—
Quinoline	31 950	5.01	13.83	6.69
3-Bromoquinoline	31 050	3.07	13.14	5.38
6-Bromoquinoline	31 200	3.13	13.84	6.07
Isoquinoline	31 300	5.31	7.62	3.63
4-Bromoisoquinoline	30 900	3.32	6.05	3.49

On irradiation, pyridine is capable of removing a hydrogen atom even from cyclohexane. Irradiation of pyridine at 253.7 nm in cyclohexane (RH) results in the formation of dicyclochexyl (R–R), 2-, and 4-cyclohexylpyridines, and 2,5-dicyclohexylpyridine in the ratio 20 : 10 : 10 : 1.[16]

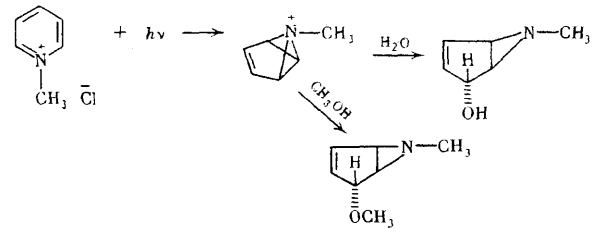


[According to our estimates the quantum yield in such a system does not exceed 2.3×10^{-4}, reaction takes place from the $S_1(n,\pi^*)$ state]. The resulting pyridine radicals can combine in the solvent cage to form dihydro-substituted compounds, recombination of which in turn leads to the formation of 2- and 4-substituted pyridines. In the presence of oxygen the yield of dicyclohexyl decreases by a factor of 10 and new products—cyclohexanol and cyclohexanone—are formed.

In a condensed state a large number of reactions involving introduction of substituents into the pyridine ring take place via the removal of a hydrogen atom by pyridine in an excited state. Thus, photoalkylation of pyridines in acid solution involves the removal of hydrogen by the nitrogen atom of a pyridine salt and the formation of the intermediates[26]

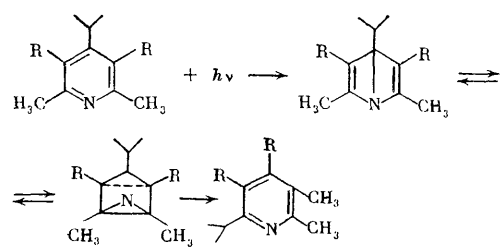


As a result of the recombination of these intermediates 2- and 4-methylpyridines, and 1-(2-pyridyl)-2-(4-pyridyl)ethane are formed. Another possible method for the photoconversion of pyridine in water and methanol is isomerisation with addition of the solvent.[16]



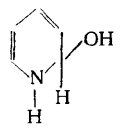
Pyridyl radicals could only be directly detected in an argon matrix. It was established that these radicals are photochemically active. On absorption of a second quantum they undergo ring-opening.[65]

The photoreduction of 3,5-dicarboxypyridines also takes place via the removal of hydrogen. Products from the photoreduction and addition of methanol (1,2- and 1,4-dihydropyridines with a hydroxymethyl group at the 2- and 4-positions) are formed in methanol. Removal of hydrogen by 3,5-dicarboxypyridines occurs in the $S_2(n,\pi^*)$ state and the resulting α-hydroxyalkyl radicals disproportionate. Malkin et al.[64] suggest that this reaction takes place via the S_2 state, since there is no correlation between the rate constants of fluorescence quenching and the photochemical reaction. In the excited $S_2(n,\pi^*)$ state of 3,5-dicarboxypyridines removal of hydrogen from the solvent as well as isomerisation to form the intermediate "Dewar pyridine" and prismane are possible. In this case photoreduction generally occurs more rapidly because of the large concentration of alcohol. However, the photoreduction of 4-isopropyl-3,5-dicarboxypyridine, whose isopropyl group gives rise to steric hindrance, does not occur, and instead of this isomerisation takes place



where R = COOH.

Pyridine decomposes very effectively on irradiation in aqueous solution;[65-67] the final product of photolysis are CO_2, ammonia, and water. The photolysis mechanism has so far not been precisely established, but it has been suggested[66-69] that on photoexcitation of the hydrogen-bonded complex that is formed between pyridine and water, radical addition of water takes place in the $S_1(n,\pi^*)$ state of pyridine at the 2- and 6-position to form the intermediate



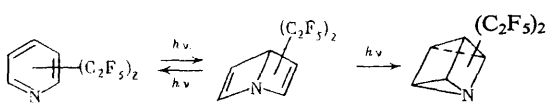
which then decomposes to give the relatively stable 5-amino-2,4-pentadienal, which has been detected as an intermediate.[65,66,70,71] However, in the opinion of Wilzbach and Raush[66] 5-amino-2,4-pentadienal is formed in water by hydrolysis of "Dewar pyridine" (2-azabicyclo[2.2.0]hexa-2,5-diene). Thus, in all of the solvents pyridine initially gives "Dewar pyridine", which is either reduced to 2-azabicyclohex-5-ene or hydrolysed to the aldehyde.[66] Photolysis of pyridine is accelerated when the pH is lowered and suppressed in an alkaline medium.[65] In general the pyridine ring is much less stable towards light than the aromatic ring of aniline, which is confirmation of the important role of *n*-electrons during photolysis.

b) Photoisomerisation. The most characteristic photolytic reaction of pyridine itself and its derivatives is photoisomerisation to form "Dewar pyridine" and benzvalene.[39] Reverse rearomatisation of these unstable isomers leads to the formation of various substituted pyridines. Isomerisation occurs both in the gas phase and in solution.[72] The product from the photolytic irradiation of pyridine in butanol at −15 °C is "Dewar pyridine", whose lifetime is almost 2 min.[72]

When pyridine is irradiated with light in an argon matrix at 8 K there is the initial formation of "Dewar pyridine", which is subsequently reduced to HCN and cyclobutene and then decomposes right through to acetylene.[72] Similar reactions of pyridine to HCN and acetylene also occur in the gas phase.

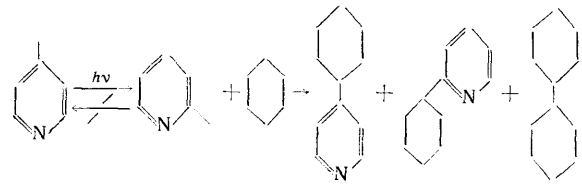
It is assumed[39] that the reversible photoisomerisation of pyridine to benzvalene occurs on excitation to the $S_2(\pi,\pi^*)$ state and it is this reaction that is responsible for the efficient radiationless deactivation of the higher excited states of pyridine in the gas phase.

As in the case of benzene, replacement of hydrogen in pyridine by a perfluoroalkyl group contributes towards the isolation of the respective "Dewar pyridines" and azaprismane in high yield:[72]



In contrast to perfluorobenzene, perfluoropyridine is light-stable. Photolytic irradiation of perchloropyridine results in cleavage of the C(3)−Cl bond, and the resulting radicals react with the solvent.[71,72]

Photolytic irradiation of 2-methylpyridine (2-picoline) in the gas phase gives 3- and 4-picolines. Irradiation of the different picoline and lutidine (dimethylpyridine) isomers results in the formation of other isomers, apparently via the formation of azaprismanes.[39,40] When 2- and 4-picolines and 3,4-lutidines are irradiated in cyclohexane, isomerisation and substitution occur,[39,73] while in the case of 2,3-, 2,4-, and 2,5-lutidines only substitution takes place:[73,74]



c) Photosubstitution. Halogen derivatives of pyridine undergo effective substitution of the halogen in water to form pyridines, the quantum yield being independent of the pH of solution. The reaction mechanism involves the heterolytic cleavage of the C−halogen bond (S_N1-type reaction) and reaction of the carbocation with water.

In the gas phase and also in heptane and methanol 2- and 3-bromopyridines when exposed to light form pyridine, while in water hydroxypyridine is formed.[71,75] In this case photosubstitution takes place via the S_1 state, in which pyridine is involved in a donor-acceptor reaction with water or other nucleophiles, resulting in substitution and induced deactivation. Substitution by hydrogen in non-aqueous solution is caused by homolytic dissociation of the C−halogen bond and removal of an H atom from the solvent by the respective radical.

The photoreduction of iodopyridine by sodium during matrix isolation leads to the formation of the respective pyridyl radicals[64] as a result of dissociative electron capture:

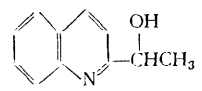
$$Na + PyX \xrightarrow{h\nu(\lambda > 500\ nm)} Na^+ + [PyX^-]^* \rightarrow Py + X^\cdot.$$

2-, 3-, and 4-pyridyl radicals have been detected. Pyridyl radicals can undergo further photochemical reactions related to cleavage of a CN bond in the aromatic ring; this frequently occurs in the direct photolysis of alkylpyridines.[64,70] The pyridyl radicals detected are σ-radicals, and the orbital which is occupied by the electron is to the extent of 70% a *p* orbital of the bond undergoing cleavage.[70]

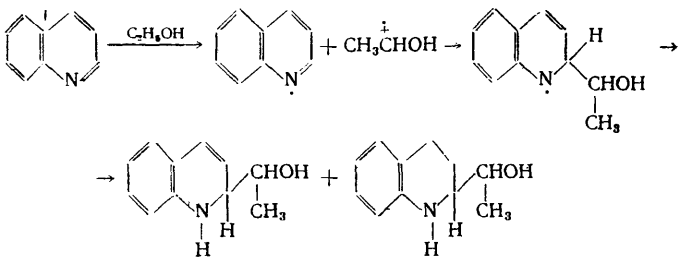
In acid media (HCl in ethanol) quinolines undergo photoalkylation to form 2- and 4-ethylquinolines. In the opinion of Stermitz et al.[76] protonated quinoline in an excited state removes a hydrogen at the β-position of ethanol so that a hydrogen atom adds on to the amine nitrogen atom. The resulting radicals react with quinoline at the 2- and 4-positions and elimination of water and rearomatisation subsequently occur, leading to the formation of alkylation products with a quantum yield of 0.02.[76] In acid solutions of isopropanol the photoalkylation of quinoline does not occur. Under these conditions the reduced forms of quinoline dimers are formed in low yield.

Photolytic irradiation of isoquinoline in ethanol in the presence of HCl leads to the formation of 1-ethylquinoline, while in isopropanol (as in the case of quinoline) photoalkylation does not occur.

Photolytic irradiation of quinoline in ethanol in the absence of acid leads to the formation of 2-(1-hydroxyethyl)quinoline:



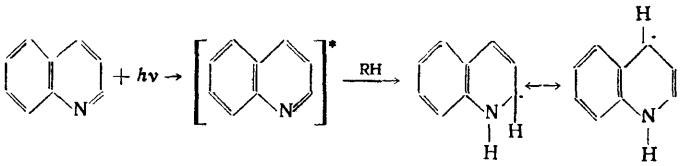
as well as traces of the 1,2,3,4-tetrahydroquinoline:



It is still not clear why substitution only occurs at the 2-position in the absence of acid.[76]

The photoalkylation of quinoline and isoquinoline in benzene also occurs in the presence of organic acids in an atmosphere of nitrogen. As in alcohols photoalkylation of quinoline occurs at the 2- and 4-positions while in isoquinoline it occurs at the 1-position. The mechanism of photoalkylation involves removal of a proton from the acid by quinoline in an excited state and formation of an exciplex. Decarboxylation of the exciplex leads to the formation of an ion pair, recombination of which gives products of reductive alkylation.[76,77]

When quinoline is irradiated in cyclohexane, 2-cyclohexylquinoline and 4-cyclohexylquinoline are formed, while in diethyl ether 2- and 4-(1-ethoxy)quinolines are formed.[67,78] Only 1-(1-ethoxy)isoquinoline is formed from isoquinoline in ether. The proposed mechanism involves the formation of unstable radicals:



Photolytic irradiation of 2-cyanoquinoline in alcohols results in photosubstitution of the CN group by OR; the same process occurs in acid solutions but with a lower quantum yield (as mentioned above, quinoline undergoes photoalkylation).[79] Sensitisation experiments show that photosubstitution occurs in the $T_1(\pi,\pi^*)$ state.

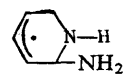
Examples of electrophilic photosubstitution of pyridine and quinoline are almost unknown, possibly because electrophilic reagents are often efficient quenchers of excited states. Moreover, it is difficult to produce a high concentration of an electrophilic reagent that is needed to carry out the reaction with a short-lived triplet state.

2. Aminopyridines and 7-azaindolines

The acid-base properties of aminopyridines and 7-azaindolines are virtually the same; the former and the latter are initially protonated on the pyridine ring (pK_a 5.8–7.1),[70,74,76] but a second protonation on the amino group occurs with difficulty. The absorption spectrum of the dication of 3-aminopyridine undergoes a hypsochromic shift relative to the monocation and neutral form (3800 cm^{-1} in water) while the fluorescence spectrum of the dication matches the fluorescence spectrum of the monocation. This is because adiabatic dissociation occurs in the S_1 state of the dication and fluorescence of the monoprotonated cation is observed.[66] This is a reflection of the general trend towards weakening of the basic properties of these heterocyclic amines in an excited state, as a result of which their cations dissociate adiabatically while neutral amines acquire the ability to fluoresce.[61,67] At the same time the acidity of the amino groups of all aromatic amines in an excited state increases, so both aminopyridines and 7-azaindolines undergo adiabatic dissociation by an acidic mechanism in the S_1 state on quenching of fluorescence with the OH^- ion.[60]

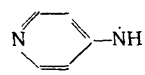
Protonation of the pyridine ring of 7-azaindolines in alcohols and water leads to a marked increase in the energy of $n \rightarrow \pi^*$ transitions compared with $^1\pi \rightarrow \pi^*$ transitions, since the proton interacts with the unshared electron pair of nitrogen in the pyridine ring. As was mentioned above, this is manifested in a sharp increase in the quantum yield of fluorescence of 7-azaindoline cations compared with the neutral compound (see Table 6). The increase in yield is due to "removal" of the $S(n,\pi^*)$ state and the absence of any possibility for intersystem crossing of the cations (Fig. 8).

When aminopyridines are irradiated, radicals of two types can be formed. It was proposed[58] that radicals that are formed by photolytic irradiation of 2-aminopyridine in cyclohexane should be regarded as of pyridyl type:

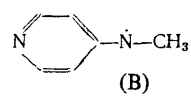


It is assumed that formation of the radical occurs in the $S_2(n,\pi^*)$ state of 2-aminopyridine by removal of a hydrogen atom from the solvent and that the NH bond is not cleaved (this conclusion was based on the absence of intermediates in the photolysis of 2-aminopyridine in methanol, ethanol, and acetonitrile).[58,68]

At the same time in the photolysis of 4-aminopyridine in isopropanol it is suggested[68] that there is cleavage of an NH bond and formation of an aminyl radical, whose absorption spectrum has a maximum at 440 nm:



It is thought that the NH bond of 4-*N*-methylaminopyridine is cleaved in isopropanol so that an aminyl radical is formed



(B)

The process takes place via an unidentified short-lived intermediate state. During photolysis in acetonitrile, the radical cation of 2-aminopyridine, whose absorption spectrum has a maximum at 500 nm, is formed in addition to (B).[57,58]

When the temperature is lowered the quantum yield for photodissociation of the NH bond decreases in all solvents and the triplet-triplet absorption of aminopyridines becomes appreciable[59,60] (this is the only case known to date of $T-T$ absorption in pyridine derivatives).

It was shown by pulsed photolysis that the photolytic irradiation of 2-aminopyridine and 7-azaindoline in all solvents leads to cleavage of an NH bond and formation of aminyl radicals, which then dimerise (Table 8).[59,60] The removal of a hydrogen atom from the solvent by aminopyridine in the $S_2(n,\pi^*)$ state as proposed by Wolleben and Testa[58] is unlikely and contradicts the results of Dvornikov et al.[59–62]

The luminescence spectroscopic and photochemical properties of aminopyridines and 7-azaindolines are very similar and this provides the basis for the assumption that on photolysis of 2-aminopyridines

cleavage of an NH bond occurs and aminyl radicals are formed from the T_1 state. The similarity of the spectra of the resulting radicals to the spectra of other aminyl radicals may serve as confirmation of this.[57,63]

The lifetime of the T_1 state of 7-azaindoline in heptane at room temperature is 1 μs and such a short lifetime is also characteristic of the T_1 state of *o*-aminopyridines.[61–63] The $T-T$ absorption spectrum could only be recorded at −155 °C, the rate constant for deactivation of the T_1 state being 381 s^{-1}.[55,56]

The quantum yield of fluorescence of 7-azaindolines does not depend on the wavelength of excitation,[67] which is also confirmation that photodissociation occurs from the T_1 state of 7-azaindolines (and not from higher excited states as in the case of amines and indoles).

Table 8. Extinction coefficients of aminyl radicals and quantum yields for photodissociation of the N–H bond of 7-azaindolines in benzene.[59–61]

Compound	ε_{rad}, mol^{-1} cm^{-1}	φ_{rad}
4,6-Dimethyl-AI*	480	0.36
4,6-Dichloro-AI	480	0.22
4-Methyl-AI	457	0.24

*AI = 7-azaindoline.

3. Acridine

The most characteristic photolytic reaction of acridines is their reduction to acridanes, which occurs with varying efficiency in all solvents. The reduction takes place via both the $T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$ states.[80] The quantum yields of the photoreduction of acridine in different solvents are given in Table 2.

The photoreduction of acridine in non-polar solvents always takes place partly by a molecular mechanism and partly by a radical mechanism.[79–82] The radical mechanism involves the removal of a hydrogen atom by acridine in an excited state from the solvent to form acridine radicals, the destruction of which leads to the formation of acridane and dihydroacridane.[81,82] The molecular mechanism involves the successive or parallel reduction of acridine at two positions [N and C(9)], but is it not clear whether photoreduction occurs as a result of a one step process or via the formation of a short-lived intermediate.[81] A study of the photoreduction of acridines in binary mixtures showed[81] that the molecular and radical mechanisms occur independently of each other from different excited states of acridine.

In aqueous solution the photoexcitation of acridine results in its photoionisation, which occurs by a mechanism involving two quanta of energy. It follows from experiments on the effect of KI on the yield of solvated electrons that photoionisation mainly occurs via the S_1 state of acridine.[82] The reaction of a hydrated electron e^- with a neutral molecule of acridine results in the formation of a neutral *C*-centred radical while the acridine radical cation (formed at the same time as e^-) is deprotonated to give an *N*-centred radical (Fig. 9).

The photochemistry of acridane (9,10-dihydroacridine) is closely related to the photochemistry of acridine. The photolytic irradiation of acridane and acridine in ethanol at 93 K and room temperature results in the formation of a radical cation (maxima in the absorption spectra at 638 and 358 nm), an *N*-radical (364 and 351 nm), and a *C*-radical (520 nm).[84] All these species are formed by a two-quantum mechanism from the T_1 state of acridane.[84]

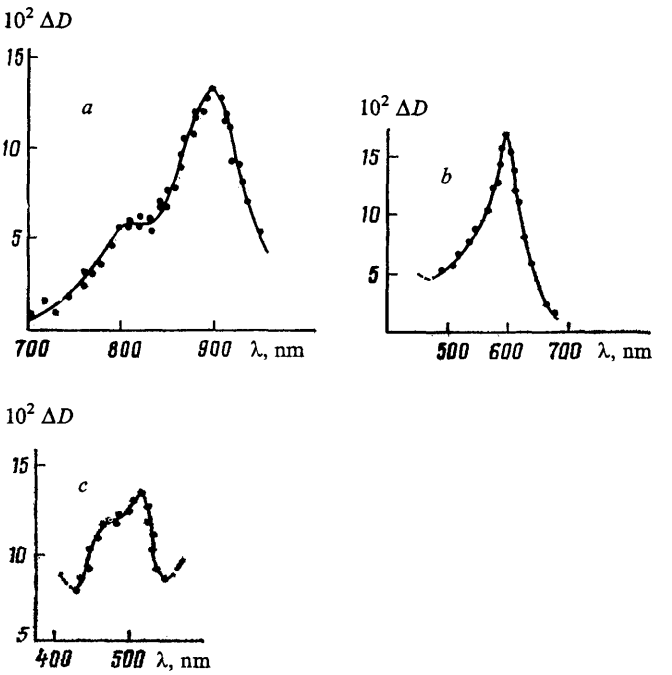
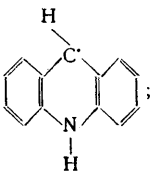
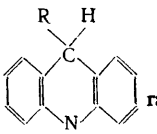
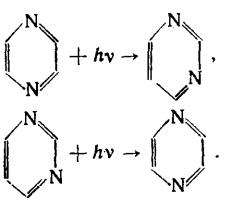


Figure 9. Absorption spectra of short-lived intermediates in the photolysis of acridine in ethanol: *a*, the acridine radical cation; *b*, the  radical; *c*, the  radical.

4. Diazines

Diazines undergo photoisomerisation in the vapour phase:[85]



The quantum yield for formation of an isomer increases with an increase in energy of excitation—by a factor of 100 for light at 253.7 nm (S_2 band) compared with light at 313 nm (S_1 band) (Table 9). Isomer formation competes with the deactivation of

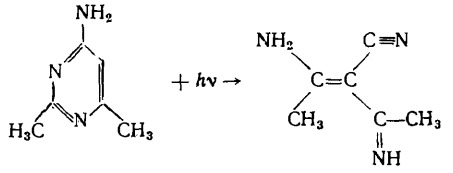
vibrationally excited molecules through collisions. The isomerisation of pyrimidine and pyrazine can be sensitised with mercury[85] but not with benzene, i.e., for photoisomerisation to occur a sufficiently high lying triplet state is required (Table 9).

Table 9. Quantum yields for photoisomerisation of diazines.[85]

Initial compound	Compound formed	φ_1^*	φ_2^{**}
Pyrimidine	Pyrazine	$(1.7\pm0.1)\cdot10^{-3}$	$(3.8\pm0.4)\cdot10^{-2}$
4,6-Dimethylpyrimidine	2,5-Dimethylpyrazine	$(4.6\pm0.4)\cdot10^{-3}$	$(3.6\pm0.4)\cdot10^{-2}$
5-Methylpyrimidine	2-Methylpyrazine	$(7\pm0.7)\cdot10^{-3}$	$(5.2\pm0.5)\cdot10^{-2}$
Pyrazine	Pyrimidine	$(7\pm0.7)\cdot10^{-3}$	$(2.8\pm0.2)\cdot10^{-2}$
2,5-Dimethylpyrazine	2,5-Dimethylpyrimidine	$(3\pm0.3)\cdot10^{-3}$	$(1.4\pm0.15)\cdot10^{-2}$
"	4,6-Dimethylpyrimidine	$(1.5\pm0.15)\cdot10^{-3}$	$(7\pm0.7)\cdot10^{-3}$

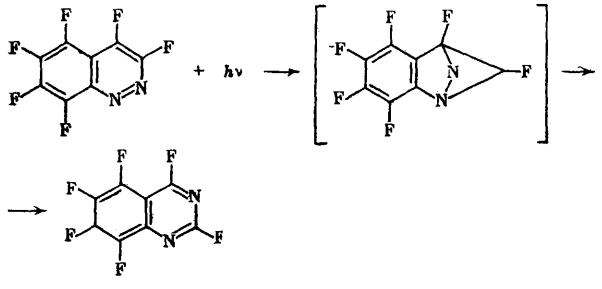
* φ_1 is the quantum yield for direct photolysis with light of wavelength 254 nm. ** φ_2 is the quantum yield for photolysis sensitised with mercury.

Perfluoropyridazine and perfluoropyrimidine are stable on irradiation at λ = 253.7 nm.[72] Ring-opening of 2,6-dimethyl-4-aminopyrimidine in aqueous alkaline solutions occurs via the formation of a "Dewar" intermediate:



The reaction product is a stable nitrile. Pyridazine undergoes photoisomerisation in the vapour phase to a mixture of pyrimidine and pyrazine, while perfluoropyridazine is converted to perfluoropyrazine, which in turn can isomerise to perfluoropyrimidine.[86] Similar reactions also occur for other fluoropyridazines and perchloropyridazine, which is converted at 77K via its $S(n,\pi^*)$ state.[72,86]

Diazines with condensed benzene rings do not undergo photoisomerisation. The only known exception to this is perfluorocinnoline, which photoisomerises to perfluoroquinazoline:



It was shown using kinetic EPR spectroscopy that pyrazine, 2,3-pyridipyrazine, and 9,10-diazaphenanthrene can remove a hydrogen atom from isopropanol when they are in the $T_1(n,\pi^*)$ state, while quinoxaline, phthalazine, phenazine, and acridine can remove an H atom when they are in the $T(\pi,\pi^*)$ state.[78]

5. Diazines with anomalous photochemical properties

As a result of the vibrational interaction between the closely situated $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ levels in azines and diazines, efficient internal conversion occurs as a rule, and these compounds do not fluoresce. When hydrogen bonds are formed, the energy of the n,π^* state increases and the quantum yield of fluorescence increases. In the majority of cases the addition of a proton also increases the intensity of fluorescence of *N*-heterocyclic compounds.[87–89]

Compounds containing a pyrazine ring (known as anomalous diazines) stand out from amongst the large number of diazines.[90] The anomalous nature of their behaviour lies in the large increase in their basicity in the S_1 and T_1 states. Moreover, in contrast to the other mono- and di-azines, the quantum yield of fluorescence and phosphorescence of the mono- and di-cations of anomalous diazines is very low (Table 10).

Table 10. Features of the luminescence spectra of diazines.[89–98]

Compound	φ_n	φ_{ISC}	Protonation I			Protonation II			Refs.
			pK_{S_0}	pK_{S_1}	pK_{T_1}	pK_{S_0}	pK_{S_1}	pK_{T_1}	
Pyrazine	0.0013	1.0	1.0	—	11.5	−6.6	—	11.1	[39]
"	0.00009	0.13	—	—	—	—	—	—	[89]
"	0.0004	0.33	—	—	—	—	—	—	[98]
Pyrimidine	0.0029	1.0	—	—	—	—	—	—	[39]
"	0.015	0.08	—	—	—	—	—	—	[91]
"	—	0.12	—	—	—	—	—	—	[95]
Pyridazine	0.0002	0.24	2.29	—	—	−7.78	—	—	[94]
"	—	1.0	—	—	—	—	—	—	[98]
"	—	0.20	—	—	—	—	—	—	[91]
Quinoxaline	0.003	0.99	0.6	4.9	5.0	−5.5	2.2	—	[92]
"	—	0.27	—	—	—	—	—	—	[96]
"	—	0.18	—	—	—	—	—	—	[97]
Quinazoline	0.0004	0.70	—	—	—	—	—	—	[96]
Phthalzine	—	0.48	—	—	—	—	—	—	[94]
"	—	0.43	—	—	—	—	—	—	[96]
"	—	0.95	—	—	—	—	—	—	[97]
Phenazine	0.006	0.76	1.21	6.0	4.0	−4.3	4.1	5.7	[52]
1,4-Diazapahenanthrene	—	—	0.9	—	6.4	—	—	—	[92]
Benzophenazine	0.0008	—	1.05	1.5	4.5	—	—	—	[93]
"	0.02	—	—	—	—	—	—	—	[93]
1,4-Diazatriphenylene	—	—	—	−0.4	6.3	—	—	—	[93]

Thus, for example, pyrazine itself is protonated in frozen solutions of H_2SO_4, and phosphorescence of its neutral (A) and mono- and di-protonated forms (AH^+ and AH_2^{2+} respectively) occurs with maxima at 26 700, 21 600, and 24 100 cm^{-1}. In the opinion of Shinada[88] and Grabowska and Pakula,[89] while in free pyrazine phosphorescence occurs from the $T_1(n,\pi^*)$ state, in AH^+ and AH_2^{2+} it takes place from the $T_1(\pi,\pi^*)(^3L_b)$ state. The electron density on the nitrogen atom of pyrazine increases with π,π^*-excitation and decreases with n,π^*-excitation (compared to the ground state). Thus, pyrazine, which is an extremely weak base in the ground state, increases its basicity in the T_1 state.[89]

In the opinion of Grabowska and Pakula,[89] all of the anomalies of pyrazine derivatives are related to the fact that the pyrazine ring in an excited state adopts a bent conformation, and the hybridisation of the N atom changes from sp^2 to sp^3. The basicity of 1,2-benz-

phenazine, like an anomalous diazine, increases substantially on excitation. Relaxation of the excited state of the 1,2-benzphenazine monocation results in the occurrence of this type of bent structure, in which the $S(\pi,\pi^*)$ state is very effectively mixed with the $S(n,\pi^*)$ and $S(\sigma,\pi^*)$ states (much more effectively than in a planar molecule). On excitation the cation of 1,2-benzphenazine is folded like a butterfly about the N–N axis, with quantum calculations showing that protonation occurs on the N(10) atom.[99] This bent structure containing two sp^3-hybridised N atoms is only formed by a pyrazine ring and not by a pyrimidine ring (this follows from an examination of molecular models[90]). On excitation there is a substantial increase in electron density in the pyrazine ring. In the S_1 state of doubly protonated 1,2-benzphenazine it is as if an additional electron has appeared, and in the case of 1,4-diazatriphenylene as if there is an increase of 1,4 electrons,[92] which results in an increase in basicity (Table 10).

A consequence of this increase in basicity is the fluorescence quenching of benzphenazine by a proton at the almost diffusion-controlled rate of 3×10^9 litres mol^{-1} s^{-1} to form a non-fluorescing dication.[100] An extremely rare phenonenon characterises the benzphenazine monocation—a dependence of the emissive deactivation constant of the S_1 state on temperature. This also reflects the change in geometry of the molecule on excitation.[100]

In other diazines that do not contain a pyrazine ring (5,12-diazatriphenylene, 1,7-diazaphenanthrene) and in all monoazines there is no such increase in electron density on excitation.

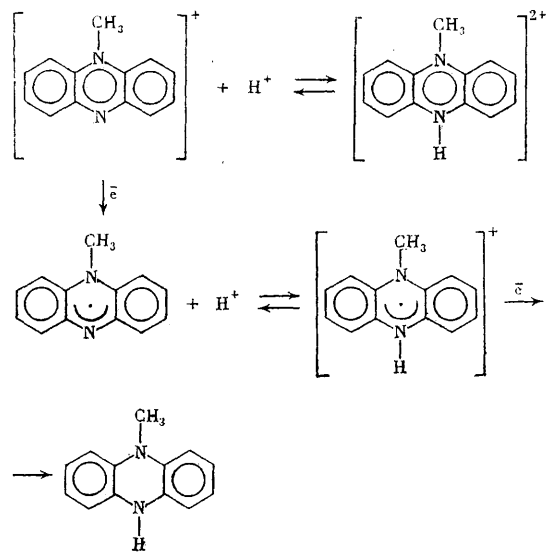
For the other (non anomalous) bicyclic diazines an absence of fluorescence from the free molecules ($\varphi_f \approx 10^{-3}$) is typical (Table 10), namely, in all these molecules only internal conversion competes with intersystem crossing. It was demonstrated using the method of optically detected magnetic resonance that for quinoxaline the lowest state is $T_1(\pi,\pi^*)$ and the intersystem degradation $T_1(\pi,\pi^*) \rightsquigarrow S_0$ occurs as a result of a strong vibrational interaction with the ground state involving the z-orbital component of spin-orbit coupling.[54] In contrast to all the remaining bicyclic diazines, the lowest triplet state of phthalazine is a mixed $T(n,\pi^*)-T(\pi,\pi^*)$ state and not a pure π,π^* state.[101,102]

Phthalazine is reduced in isopropanol to form 1,2-dihydrophthalazine and its dimer 1*H*,1′*H*,2*H*,2′*H*-1,1-diphthalazine.[103] Photoreduction occurs through the removal of an H atom from isopropanol by phthalazine in the S_1 state to form 1,2-dihydrophthalazine with a quantum yield of 0.013. At the same time phthalazine undergoes dimerisation in the T_2 state with a quantum yield of 0.040. The photoalkylation of phthalazine occurs in alcohols on treatment with acids.[103]

6. Phenazine

During photolysis in the absence of oxygen, phenazine (in the same way as acridine) undergoes photoreduction to dihydrophenazine. In the presence of oxygen there is complete recovery of the initial phenazine. The quantum yield of the overall reduction of phenazine in toluene is 10^{-3} and in tetrahydrofuran the yield is 6×10^{-2}. A molecular complex between phenazine and dihydrophenazine which is in equilibrium with the initial reactants has been detected.[104] From an analysis of the dependence of the quantum yield of photoreduction on the concentration of tetrahydrofuran it was possible to conclude that the two lowest $T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$ states of phenazine participate in this process.[104,105] The decrease in quantum yield of photoreduction in the presence of eosin, which is accompanied by a triplet-triplet absorption of phenazine, indicates that photoreduction occurs at least partly via the $T_1(\pi,\pi^*)$ state. This is also confirmed by the sensitisation of photoreduction with diacetyl and the quenching of this process with oxygen. The rate constants for removal of an H atom from tetrahydrofuran by phenazine in the $T_2(n,\pi^*)$ and $T_1(\pi,\pi^*)$ states are equal to 1.5×10^7 and 4×10^3 litres mol^{-1} s^{-1} respectively. The quantum yields for photoreduction of phenazine in methanol, ethanol, and isopropanol on exposure to light at 365 nm are 0.023, 0.037 and 0.050 respectively.[104]

It was established by EPR spectroscopy and spectrophotometry that during photoalkylation of phenazine the methylphenazinium cation undergoes photoreduction in isopropanol on irradiation at 405 nm to form the stable methylphenazinyl radical and its radical cation. This radical exhibits a characteristic fluorescence with a maximum at 14 200 cm^{-1} and lifetime of 5.1 ns. In addition, the methylphenazinium cation undergoes dealkylation to free phenazine and the radical cation is later reduced to dihydrophenazine.[106] The ratio of the processes involving dealkylation and reduction to the radical depends on the steric properties of the alcohols (solvents). Dealkylation does not occur in isopropanol, while in methanol and ethanol the efficiency of both processes is comparable. The pK values of alkylated phenazines and their radicals have been determined:[106]



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The presence of an unshared electron pair that does not participate in conjugation in six-membered azines leads to a fundamental difference between the features of the luminescence spectra and photochemistry of azines and those of the aromatic amines examined by us previously.[83] For heterolytic amines photoreduction and cleavage of bonds in the ring are typical. In almost all azines there is a vibrational interaction to a given extent, resulting in a mixing of the closely situated n,π^* and π,π^* states (the proximity effect), which generally increases the probability of radiationless deactivation of the excited states. Therefore the formation of hydrogen bonds and protonation, which assists the destabilisation of the n,π^* states and "removes" this type of vibrational interaction, always substantially alter the luminescence properties, leading as a rule to an increase in the quantum yield of fluorescence.

Heterocyclic amines, like aromatic amines have quite a low ionisation potential and participate in photoionisation and photooxidation, but on the other hand they have a set of properties characteristic of aromatic compounds (the capacity for photosubstitution, photoisomerisation, etc.). The ability of the NH bond to undergo dissociation is also common to all classes of amines.

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Recent trends in the theory of the deamination of aliphatic and alicyclic amines

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ABSTRACT. The different theories that account for the stereochemical characteristics of the deamination of aliphatic and alicyclic amines compared to solvolysis of the corresponding sulphonates and halides are examined. There is a discussion on the recent hypothesis concerning the relative increase of electron demand for the participation of neighbouring groups and bonds in deamination compared to solvolysis, making it possible to predict the direction of skeletal rearrangements in reactions involving elimination of nitrogen and to carry out deliberately such rearrangements when they do not occur in reactions with classical leaving groups. Questions concerning the applicability of the extended Hammond postulate and the Curtin–Hammett principle to reactions that involve decomposition of alkyldiazonium ions are discussed.

The bibliography includes 73 references.

Contents

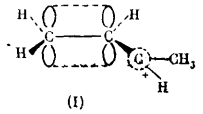
I. Introduction 179
II. Theory of the increase in electron demand for participation in S_N1-deamination compared to S_N1-solvolysis 180
III. A critical examination of the literature data on a comparative study of deamination and solvolysis 185
IV. The Hammond postulate and Curtin–Hammett principle applied to a comparative study of deamination and solvolysis 187

I. Introduction

During the past thirty years hundreds of articles devoted to a comparative study of deamination and solvolysis have been published. There have been a number of reviews in which this question has received special attention.[1–6] The present review, without claiming to be complete, makes an attempt to interpret the results reported earlier in terms of a new hypothesis that has recently been developed concerning the relative electron demand for participation of neighbouring groups and bonds in S_N1-decomposition of aliphatic and alicyclic diazonium ions.[7,8]

The steady interest in what appears at first glance to be a special problem is maintained not only by the contradictions existing to date in the interpretation of the experimental results but also by the close link with the basic concept of carbocations and the debate about nonclassical ions as well as with such fundamental theories as the Hammond postulate and the Curtin–Hammett principle. The above-mentioned hypothesis interprets the application of these postulates to aliphatic deamination in a new way. Moreover, for a long time the theoretical aspect of the problem has relegated the synthetic possibilities of deamination to second place. Meanwhile, the "driving force" of the rearrangements in such reactions is much higher than in traditional solvolysis and it would be tempting to learn how to regulate this process.

It may be assumed that the synthetic use of deamination has been held in check not so much by the widespread notion of the supposed low selectivity of reactions involving the elimination of nitrogen as by the long absence of an adequate theory that has predictive force in relation to stereochemistry and the composition of the products of such reactions in alicyclic compounds and particularly in aliphatic compounds. In the 1950's the concept of "hot" ions was put forward by a number of authors. This hypothesis, which qualitatively accounts for the "unconventional" rearrangements during deamination, has been followed in various forms in many publications. Various factors have been identified as the source of excess energy. Thus, the high stability of the nitrogen molecule must assist the large exothermicity of the reaction. In turn, it is possible with this hypothesis to conclude that there is "chemical activation" of the carbocations as reaction products. It was suggested that there is non-optimal solvation of the carbocations during rapid decomposition of a diazonium ion. Abnormal charge localisation in relation to the non-optimal geometry of the carbocation has also been proposed, as for example in one of the precursors of all "hot" ions—the hypothetical nonconjugated allyl cation (I):[9]



(I)

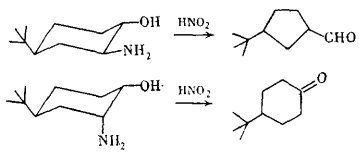
On the strength of this, the terms "localised", "free", and "open" carbocations have appeared in the literature together with the term "hot". These terms signify at the same time the classical nature of carbocations from deamination (as opposed to nonclassical cations from solvolysis) as well as the excess energy contained in them. There has been a lively discussion of the concept of "hot" ions in the literature, while, at any rate, for a long time two factors do not seem to have been in doubt—the classical nature of carbocations from deamination and the absence of any S_N2 activity in this reaction.

The ease in forming molecular nitrogen and the probable low energy of activation related to this led to the idea of a "compression" of the energy scale. This hypothesis, which belongs to Huisgen,[10] does not require the concept of a "hot" ion since the reduction in the difference in energies of activation between the competing routes for forming carbocations—processes involving

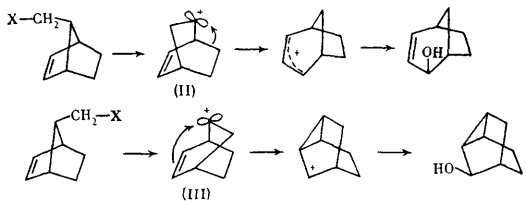
neighbouring groups and bonds (k_Δ) and with assistance from the solvent (k_s)—favours a reduction in selectivity in the choice of routes for forming carbocations as compared to traditional solvolysis. It is easy to see that by using these concepts it is impossible to predict the stereochemical result of a reaction.

It soon became clear that one of the main problems with the idea of "hot" ions is its failure to account for the differences in product composition that occur in the deamination of cyclic diastereomeric amines. For example, if in Scheme 1 the sole intermediate species is the 2-hydroxy-5-t-butylcyclohexyl cation, the reason for such a marked difference in the results of the reaction[11] remains unclear.

Scheme 1



It was shown that this type of structural selectivity is characteristic of deamination[12] to an even greater degree than solvolysis:[13–15]

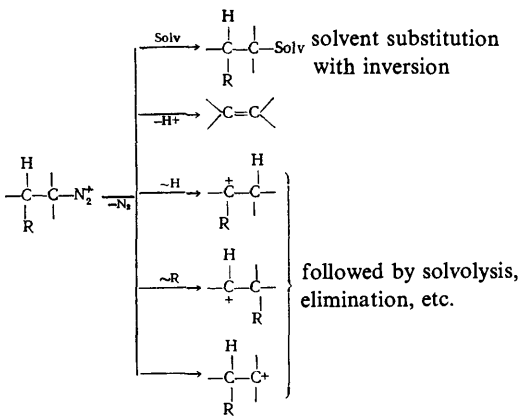


X = ONs, NH_2.

As a result, opinions that were developed from earlier ideas began to be formed. For example, the so-called "memory effect" is actually an extension of concepts such as the "localised" allyl cation to alicyclic ions. Structures (II) and (III) depict such "twist" cations.

However, it is not difficult to see that such a selective interaction of the cation site with a particular bond resembles anchimeric assistance. Streitwieser came closest to this standpoint when he put forward a familiar scheme of reaction pathways of the diazonium ion (Scheme 2).[16,17] However, he did not regard the synchronous shift of the periplanar group as a factor that assisted decomposition of the diazonium ion. In his opinion the shifts of the hydrogen atoms and alkyl groups cannot be regarded as participation in the sense that the neighbouring group can "push" the departing nitrogen but this process should more accurately be regarded as the neighbouring periplanar group being "pulled" by the departing nitrogen[16] or positively charged region which develops on the α-carbon atom.[17]

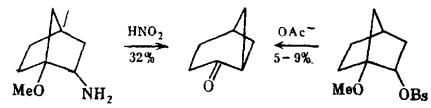
Scheme 2



The view of Streitwieser, which was developed as an alternative to the concept of "hot" ions, was criticised (see two reviews[6,18]). It is held that the scheme of Streitwieser was disproved by Collins, who demonstrated that the shift of a neighbouring group to a cation site in a number of cases occurs after the nitrogen has left the molecule (discussed in detail in Section III). In the long run Streitwieser's view was relegated to second place and for a long time was not regarded as promising. The concept of conformational control and "counterion control" became prominent (discussed in Section IV).

With the exception of the "hot" ion concept, all the remaining views are in agreement that during deamination the group that is periplanar to the nitrogen being eliminated mainly migrates. This is important in so far as it can predict the expected direction of skeletal rearrangement in relation to the configuration or conformational composition of the diazonium ion.

However, the above-mentioned concepts are insufficient because they do not shed any light on the causes of the observed rearrangements. While the concept of "hot" ions contradicts many facts and is inaccurate, it remains unclear what exactly causes the neighbouring periplanar bond to migrate during deamination. The same bond is much less prone to rearrangement in solvolysis of the analogous sulphonate:[19,20]



Facts such as these have been increasingly accumulating in the literature (see Section II), but approaches to the solution of this problem have only recently come to light—during a discussion about nonclassical carbocations, in particular, the 2-norbornyl cation.[7] The interest in deamination within the scope of this problem arises in particular because decomposition of diazonium ions was thought for a long time to be the most reliable method of generating classical ions with a "short" lifetime. However paradoxical this may be, it was the use of deamination as a model reaction for studying the property of classical cations that in the long run made it possible for serious contradictions to be revealed. The solution of these led to formulation of the hypothesis that during deamination, when compared to solvolysis, the electron demand for neighbouring group participation as a most important factor determining the stereochemistry in reactions involving elimination of nitrogen is maintained[7] or even increased.[8]

II. Theory of the increase in electron demand for participation in S_N1-deamination compared to S_N1-solvolysis

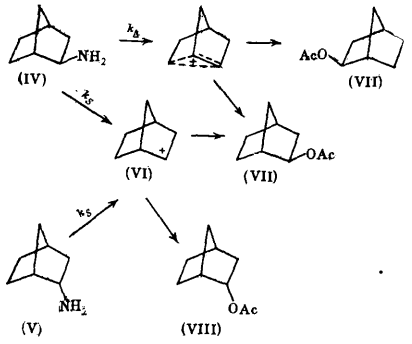
In the debate about the structure of the 2-nornbornyl cation ideas about the mechanism for deamination of epimeric 2-norbornylamines have undergone fundamental changes during the last 25 years. They can be illustrated by three studies, each of which constitutes a particular stage in the solution of the problem.

Initially Corey et al.,[21] by studying the deamination of optically active epimeric 2-norbornylamines (IV) and (V) with sodium nitrite in acetic acid, analysed the combined mixture of acetates, obtained

after reduction and acylation of the initial reaction mixtures, which contained not only acetates but also alcohols. This method of analysis, which was typical of the early studies in this area, led the authors to the mistaken conclusion that there was an approximately equal ratio of *exo*- to *endo*-products, retention of optical activity for the reactions of both amines, and hence a common intermediate—the classical cation (VI).

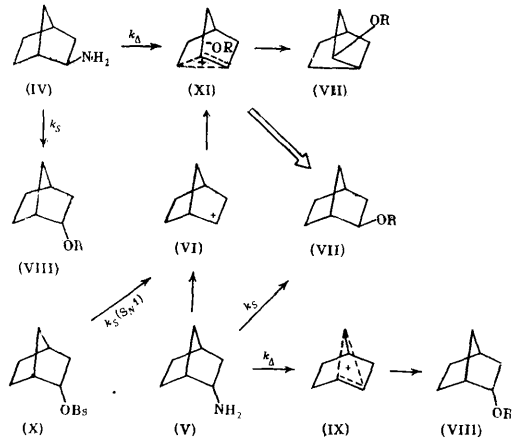
Berson et al.[22] subsequently studied in greater detail the composition of the acetate fractions that were isolated from the initial reaction mixtures, and they came to the conclusion that the assumption by Corey of a common intermediate for all products was incorrect since the degree of racemisation for *exo*-product (VII) and *endo*-product (VIII) was not the same. The values obtained for the acetate fractions were more in line with the reactions occurring according to Scheme 3. The relatively low ratios of *exo*- to *endo*-products [(VII):(VIII) ranging from 19:1 to 45:1] and the partial retention of optical activity suggest at first glance that there is a reduced degree of σ-participation in deamination compared to solvolysis, where this ratio is ~300:1 and racemisation occurs.[23]

Scheme 3



Finally, Kirmse et al.[7] recently once again carried out a similar study using a wide range of media. By varying the polarity of the medium it was possible to establish that different routes—k_Δ and k_s (the latter was of two types: S_N1 and S_N2)—were competing in the decomposition of diazonium ions (Scheme 4).

Scheme 4



The formation of *endo*-alcohols (or esters) (VIII) increases for the *exo*-amine (IV) and decreases for the *endo*-amine (V) as the polarity of the medium is reduced. This is an indication that the *endo*-products (VIII) are formed from the epimeric amines by different reaction routes. The *endo*-products (VIII) are probably formed from *exo*-amine (IV) by an S_N2-type of route k_s, but they are formed from *endo*-amine (V) by the k_Δ route since an S_N1 mechanism is preferred when there is an increase in polarity of the medium. According to Kirmse and Siegfried[7] the classical cation (VI) can be excluded for the reason that in an aqueous medium which is favourable for an S_N1 mechanism there is the highest proportion of *endo*-attack on the chiral intermediate by the nucleophile. This intermediate may be the nonclassical carbocation (IX), which is formed as a result of participation of the C(1)–C(7) bond.

The question arises: what is the reason for this participation, which does not occur in solvolysis of the analogous sulphonate? Kirmse suggests that the k_Δ process usually has the lowest energy barrier and therefore frequently occurs in solvolysis. If the k_Δ route is accompanied by an increase in steric strain in the ring, as in the case of ion (IX), the k_s process becomes energetically more favourable and it is the only one to take place in solvolysis of the corresponding *endo*-brosylate (X). However, *endo*-amine (V), which reacts when there is "compression" of the energy scale, proves to be capable of reacting by the less favourable k_Δ route. Although Kirmse and Siegfried[7] consider that this situation is an exception to the general rule, it should be recognised that the conclusion made by them can be formulated as a hypothesis about the increase (if only in certain cases) in the degree of σ-participation in deamination compared to solvolysis. However, the authors only note that the study they carried out does not support the idea of a classical 2-norbornyl cation as the precursor of *endo*-2-norbornyl products.

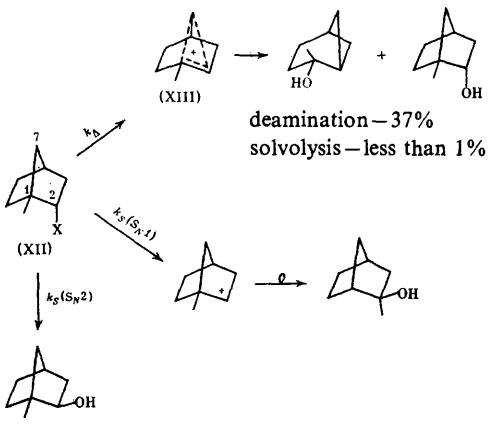
For the deamination reactions of *exo*-amine (IV), Kirmse and Siegfried[7] concluded that the reactions occur by the k_Δ route via the nonclassical carbocation (XI), which is incorporated in an asymmetric ion pair, resulting in a preferred *exo*-attack by the nucleophile on the site of nitrogen elimination. However, it is noted here[7] that from the data obtained it is not possible to make a definite choice between the nonclassical carbocation structure (XI) and a rapid equilibrium involving "*exo*-selective" classical cations.

The alternative stated above is typical of the debate about the structure of the 2-norbornyl cation and we are convinced that it is predetermined by the choice of model compound, since 2-substituted norbornanes have a number of basic disadvantages in this capacity. The most important of them are: the Wagner–Meerwein rearrangement on elimination of 2-*exo*- as well as 2-*endo*-substituents in many cases only occurs with displacement of the C(1)–C(6) bond, resulting in the initial norbornane system; the directions of attack by the nucleophile coincide for the nonclassical 2-norbornyl cation (for stereoelectronic reasons) and for the classical 2-norbornyl cation (for steric reasons); the classical cation readily changes to the nonclassical; finally, a quantitative determination of the degree of epimeric purity of the initial compounds appears quite difficult.[1,8]

However, the introduction of very simple substituents (for example, methyl groups) into the skeleton of the same norbornane makes the model more convenient. A comparison of the results of deamination and solvolysis of 1-methyl-2-*endo*-substituted norbornanes with structure (XII), as a result of the 1,2-shifts of the C(1)–C(7) bond that occur (Scheme 5), clearly indicates a considerable σ-participation of this bond in deamination (water) but not

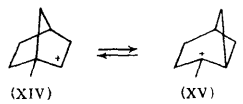
in solvolysis (aqueous acetone)†.[24]

Scheme 5



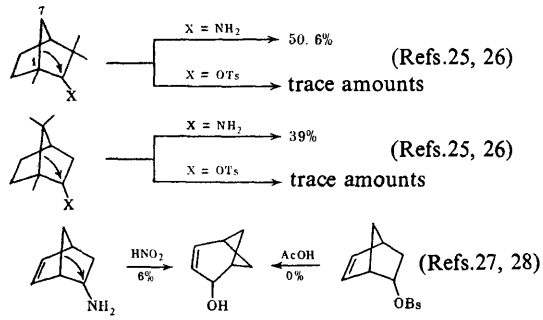
X = NH_2; *p*-$OSO_2C_6H_4$–...–...Me, –Br, –NO_2

The important role of the nonclassical carbocation (XIII) in this deamination reaction follows from the direction of attack by the nucleophile on the *endo* side and also from the very low probability of an "imitation" of cation (XIII) by rapid inter-conversion of two completely different ions — the secondary (XIV) and tertiary (XV):

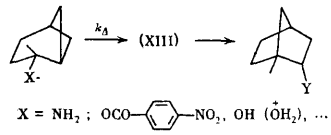


The case studied by Kirmse et al.[24] is also classed as an exception to the rule. However, 1,2-shifts of the C(1)–C(7) bond are not rare for deamination, but they hardly ever occur in solvolysis of norbornyl derivatives. Solvolysis leads to a displacement of the C(1)–C(6) bond without dependence on the configuration of the leaving group. In deamination, on the other hand, there is a clear dependence of the direction of the skeletal shift on the configuration of the leaving group, which suggests the idea of an increase in demand for the participation of neighbouring periplanar bonds in the elimination of nitrogen. A certain amount of conjecture about the change in demand for participation when going from solvolysis to deamination of compounds with a bicyclo[2.2.1]heptane skeleton gives Scheme 6,‡ which depicts a number of similar examples in outline.

Scheme 6



It should be mentioned that the reverse rearrangement of the norpinane skeleton to norbornane occurs with the same ease in both solvolysis and deamination; in this case every indication is that participation of the C(1)–C(7) bond occurs:[29]

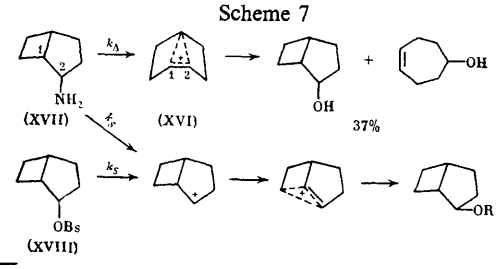


A number of problems may arise here. For example, why should the compression of the energy scale during deamination and the lack of this during solvolysis occur only in rearrangements of the type "norbornane–norpinane" and not in the reverse rearrangement or in rearrangements of *exo*-amines and sulphonates in the norbornane series. Then, if the examples of rearrangements of the type "norbornane–norpinane" given above are the exception, what should be considered the rule?

In the meantime these questions can be eliminated if it is assumed that during deamination there is an increased demand for the participation of the neighbouring periplanar band in any structures. In fact, the relative increase in the proportion of k_Δ in deamination is exhibited not only in models with a bicyclo[2.2.1]heptane skeleton.

For example, the "σ-route" to the nonclassical cation (XVI) can occur in deamination of amine (XVII) but not in solvolysis of the analogous brosylate (XVIII)[30] (Scheme 7). Kirmse et al.[30] also account for this phenomenon as an exception to the general rule. The bridging ion (XVI) is sterically unfavourable and is formed during deamination only as a result of "compression" of the energy scale together with products from the more "favourable" k_s process. In the case of solvolysis, where the k_Δ and k_s processes differ in energy much more considerably, it is only the k_s route, which is more favourable for this structure, that occurs.

Scheme 7



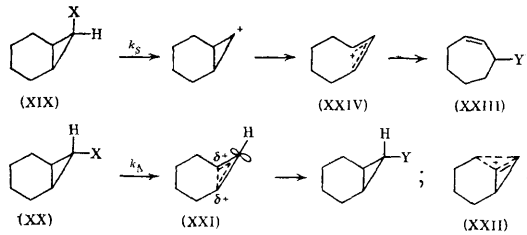
† Unfortunately, a comparison of solvolysis and deamination in the same solvents is seldom to be found in the literature. However, in our opinion, the significant differences that occur on going from solvolysis to deamination cannot solely be due to medium effects.[8]

‡ See also Scheme 5 and the reactions at the end of Section 1. The corresponding *exo*-epimers react almost exclusively with a shift of the C(1)–C(6) bond in both reactions.

It may be assumed, however, that the reason for the formation of the clearly sterically hindered carbocation (XVI) is the strong demand for participation in deamination and not "compression" of the energy scale. The latter may be illustrated by the following example.

The *endo*-tosylate (XIX), in which participation of the neighbouring carbon-carbon bonds is impossible because of the skeletal structure, reacts more rapidly than the *exo*-isomer (XX),[31] although in the latter participation of a C–C bond is probable, judging by the selectivity of nucleophilic attack (Scheme 8)§.

Scheme 8



X = NH_2; OTs, Cl, ... Y = OH, Br, OMe, OAc.

Thus, for this skeleton the barrier for the k_Δ process is definitely higher than the barrier for k_s, which, following the logic of Kirmse, unites this case with the previous one (Scheme 7). However, both solvolysis[31] and deamination[32] of compounds with the skeleton of (XIX) and (XX) give the same results for each of the epimers. Meanwhile, "compression" of the energy scale ought to lead to the formation of a considerable proportion of product (XXIII) in deamination of amine (XX), which in actual fact does not occur. The impression is created that participation of the neighbouring bonds assist to the same extent the "difficult" elimination of both the sulphonate group and nitrogen and starts to occur much earlier than the moment when the developing cation site may be stabilised by the formation of the allylic system (XXIV).

It is necessary to develop a more detailed hypothesis about the relative increase in demand for participation in deamination and substantiate the possible reasons for such an increase. Manuilov and Barkhash[8] made a comparative study of solvolysis and deamination of model sulphonates with tetrafluorobenzobicyclo[2.2.2]octadiene and tetrafluorobenzobicyclo[2.2.2]octene skeletal structures and obtained quantitative data that characterised the contribution of the k_Δ process in each reaction (one of the examples is shown in Scheme 9).

The following rules were established:

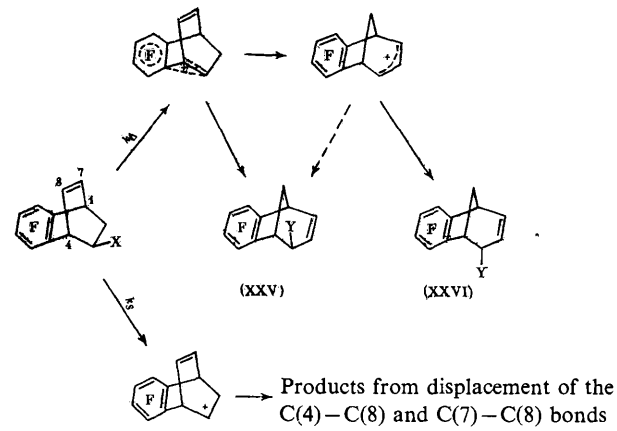
1. The preferred direction of the skeletal shift in both reactions is determined by the configuration (*exo*- or *endo*-) of the group being eliminated.

2. Selectivity in the choice of the direction of rearrangement and nucleophilic attack increases as the solvating power of the medium towards cations decreases (in the series DMSO > MeOH > AcOH). In this case the stereoselectivity of nucleophilic attack (ratio of *exo* to *endo* products) is substantially higher for deamination.

§Sliwinski et al.[31] propose the nonclassical structure (XXI). In our opinion the nonclassical carbocation (XXII) is more probable. In any case it is significant that the *exo*-isomers (XX) react by the k_Δ route while the *endo*-isomers (XIX) react by the k_s route in both reactions.

3. Comparison of the mixtures of acetates from deamination with solvolysis products generally indicates a relative decrease in the contribution of the k_Δ process in the case of deamination (agrees with Berson's results on acetate products from deamination[22]).

Scheme 9



medium—AcOH; *exo*/*endo* = (XXV)/(XXVI);
X = NH_2, Y = OH: $k_\Delta = 86 \pm 5\%$, *exo*/*endo* = (79%)/(2%)
X = OTs, Y = OAc: $k_\Delta = 89 \pm 6\%$, *exo*/*endo* = (51%)/(32%).

4. The alcohol fractions of the deamination products show a reverse trend. The relative contribution of the k_Δ process in deamination generally does not decrease or even increases compared to solvolysis (contradicts Berson's results but is in agreement with Kirmse's results[7,24,30]).

5. Nucleophiles have a greater tendency to attack the site of nitrogen elimination in deamination reactions, which may be due to the formation of an asymmetric ion pair (agrees with the conclusions of Kirmse and Siegfried[7]).

The rules established are interrelated and do not contradict each other as may appear at first glance. It is likely that with an S_N1 mechanism for the same model there cannot occur a relative decrease in the contribution of k_Δ in the case of the acetate products from deamination and at the same time an increase in contribution of this process for alcohol products. It is probable that the acetates are formed to a considerable extent by an S_N2 mechanism, so comparison of demand for participation should be carried out only "within" the S_N1 routes of solvolysis and deamination, this condition being more consistent with the alcohol fraction for the latter reaction.

In order to explain the rules propounded above from a single standpoint, it must be assumed that the observed increase in the share of the k_Δ process and the stereoselectivity of nucleophilic attack in deamination results from the increase in demand for participation in the S_N1 process of nitrogen elimination compared to a similar elimination of sulphonate or other group. The main reason for this may be a less favourable solvation of the transition state and carbocation (more precisely, cation site) in the more rapid process of decomposition of the diazonium ion. The idea of a less favourable solvation within the intimate ion pair is not inconsistent since at the moment that it is formed within the solvation cage the counterions

are separated by a nitrogen molecule (Scheme 10, compare with three studies[18,33,34]).

Scheme 10

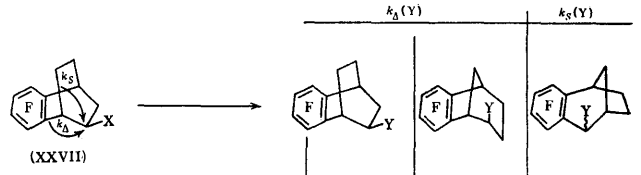
$$2HNO_2 \rightleftarrows N_2O_3 \xrightleftharpoons{Solv-OH} Solv-ONO + HNO_2;$$

$$R-NH_2 + Solv-ONO \rightarrow R-\overset{+}{N}H_2-N=O\ldots Solv-O^- \rightarrow$$

$$\xrightarrow{\sim H^+} R-\overset{+}{N}H=N-OH\ldots Solv-O^- \xrightarrow[-N_2]{\sim H^+} R^+\ldots N_2\ldots H_2O\ldots Solv-O^-.$$

The formation of a cation site in deamination as against solvolysis is comparable, if not to gas-phase conditions, at least to substantially less nucleophilic conditions, namely, it corresponds to a considerable reduction in the solvating ability of the medium. In this case deamination in AcOH, for example, should give the same stereochemical result as solvolysis does in a much more ionising and less nucleophilic medium such as CF_3COOH. This actually occurs (Scheme 11). In this case, as was to be expected, the reactions of the model compounds (XXVII) demonstrate the relative increase in contribution of k_Δ on going from solvolysis to deamination in the same medium ($\sim$49% k_Δ in acetolysis compared to 82% k_Δ in deamination in AcOH).[8]

Scheme 11



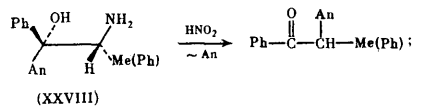
(XXVII)

	k_Δ(Y)	k_s(Y)
(Ref.8) X=NH_2 in AcOH, k_Δ=82±1%:	59%(OH)	22%(OH)	14%(OH)
(Ref.35) X=OTs in CF_3COOH, k_Δ=75±4%	45% ($OCOCF_3$)	25% ($OCOCF_3$)	21% ($OCOCF_3$)
(Ref.35) X=OTs in AcOH, k_Δ=49±6%	19%(OAc)	15%(OAc)	37%(OAc)

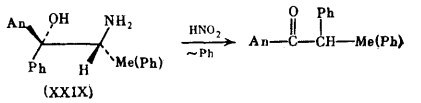
The special conditions for elimination of nitrogen probably have the result that the electrons of the neighbouring periplanar bond ("internal nucleophile") gain an advantage in attack on the cation site over any other nucleophile. In this case the demand for participation may be so great that the determining role is played not by the migrating ability of the participating group but its optimal orientation relative to the developing cation site, namely, a periplanar position in relation to the C–N bond in a given conformation or configuration.

This property of diazonium ions is widely known since it "violates" the Curtin–Hammett principle in the case of pinacolic deamination (Scheme 12).[36,37]

Scheme 12



(XXVIII)



(XXIX)

An = *p*-$MeOC_6H_4$.

In solvolysis the ratio of products formed from the different conformations of the substrate does not depend on the relative populations of the conformations and is determined solely by the free energies of the transition states leading to these products. In deamination this rule does not apply. Thus, diastereomer (XXVIII) reacts with preferred migration of anisyl while migration of phenyl is typical for diastereomer (XXIX). As Kirmse notes,[2] the nucleophilicity of the aryl group is not a factor that regulates the choice of migrant (the migrating ability of anisyl is higher in reactions with neighbouring-group participation). The ratio of products is determined by conformational control—from the most stable conformer with a *gauche*-orientation of OH and NH_2 groups stabilised by intramolecular hydrogen bonding.

This definition of conformational control in deamination is typical. In our view the electronic and conformational factors are incorrectly contrasted here, which on the whole is typical for many publications¶. It is more accurate to say that electronic factors assist the exhibition of conformational control. Among the former the demand of the cation site prevails over the nucleophilicity of the migrant. The concept of conformational control in deamination acquires a logical basis from such a statement.

If it is assumed that anchimeric assistance compensates the insufficient solvation of the cation site in decomposition of a diazonium ion, the retardation of 1,2-shifts at the stage of the nonclassical ion becomes clear. It is advantageous for a poorly solvated carbocation to preserve a nonclassical delocalisation and, moreover, the lifetime of an intimate ion pair within the solvation cage (see Scheme 10) may be relatively short. This corresponds to an increase in the ratio of *exo*- to *endo*-products in the reaction mixtures. The lack of symmetry of the intimate ion pair results in preferred attack on the site of nitrogen elimination.[7,8]

This explanation does not contradict the fact that in the acetate fractions of deamination products there is sometimes a relative increase in the share of the k_s process compared to solvolysis. In our opinion this occurs not because of a suppression of the k_Δ process for some reason "within" an S_N1 mechanism for forming acetates but is related to the increase in the relative role of an S_N2-type of k_s process that is typical for charged nucleophiles, including the acetate anion†. Thus, the theory of the increase in demand for participation in deamination compared to solvolysis applies only to S_N1 routes of both reactions.

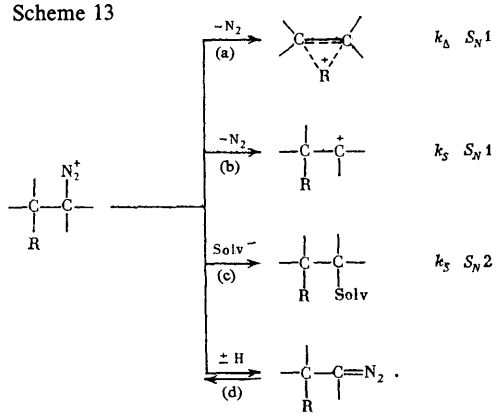
The theory advanced above can be summarised with the help of Scheme 13. The ratio of contributions of the competing routes (a)–(c) depends on the structure of the aliphatic part of the diazonium ion, the nucleophile, and the solvent. However, compared to solvolysis, the increase in demand for participation in deamination must always lead to a more effective shift of the neighbouring bond under conditions where the analogous sulphonates are often only able to react by an S_N2 mechanism. Hence the observed "reduction in selectivity" on going from solvolysis to deamination. On the other hand, the increase in electron demand makes it possible in deamination reactions to observe the shift of groups and bonds

¶ For example, in relation to the reactions of diastereomers (XXVIII) and (XXIX) Morrison and Boyd mention that the course of the reaction is determined more by conformational factors than electronic.[38] A similar but more expanded view is given by Bundel' et al.,[39] who assume that since the energy required for cleavage of the C–N bond is not great and lies within the conformational barriers, in the decomposition of the diazonium ion the determining factor for the choice of a particular conversion route is the initial confor-mation, in contrast to solvolytic reactions where the main role in this choice is played by the neighbouring group.

† For S_N2 processes in the decomposition of diazonium ions, see the studies of Kirmse[5] and Collins[6] and the references in them.

that do not migrate in solvolytic reactions. Hence, using this approach it is possible to explain satisfactorily not only the increased tendency towards rearrangements in deamination reactions, which is a well-known fact, but also to carry out rearrangements intentionally in those cases where the conformational composition (or configuration) of the initial amine is reliably known.

Scheme 13

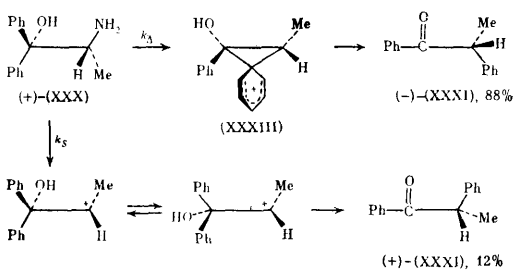


III. A critical examination of the literature data on a comparative study of deamination and solvolysis

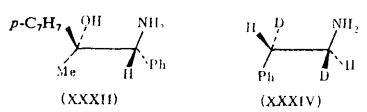
In accordance with Schemes 2 and 13 the diazonium ion is the "branching point" in the competing pathways of deamination. As was mentioned above, Collins published a number of studies (see his review[18]) in which the scheme of Streitwieser is criticised. It is therefore necessary to examine the arguments of Collins in relation to the new Scheme 13.

In deamination of the optically active amine (+)-(XXX) in acetic acid, an appreciable quantity of product (+)-(XXXI) is obtained, being formed as a result of migration of a phenyl group to the cation site obviously after the nitrogen has left the molecule (Scheme 14).[40–42]

Scheme 14



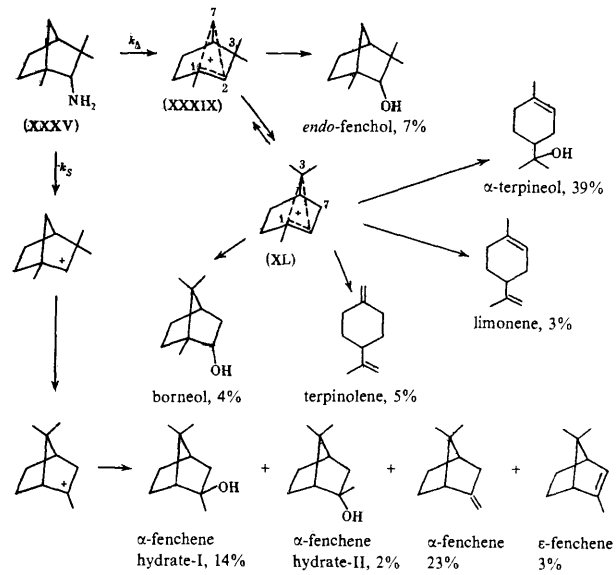
Retention of configuration is even more substantial (58%) compared to inversion in the case of the deamination of amine (XXXII) in the same medium.[42]



In the opinion of Collins these results contradict the postulate of Streitwieser that the diazonium ion prior to the carbocation serves as a branching point of the competing reactions, since the displacement of the neighbouring group occurs after the change in conformational state of the carbocation. In actual fact there is no contradiction with Scheme 13, as the formation of product (+)-(XXXI) corresponds to route k_s(b). However, at least a proportion of compound (−)-(XXXI) may be obtained by route k_Δ(a) via the phenonium ion (XXXIII) (Scheme 14). If the amino group is situated on a benzyl carbon atom rather than a secondary carbon atom, the k_s(b) process successfully competes with the k_Δ process. This specific example cannot, of course, be extended to deamination as a whole as Collins has done, assuming that "migration of hydrogen or aryl... in most cases occurs after decomposition of the diazonium ion."[18] For example, it is not surprising that in the reaction of the optically active amine (XXXIV), which has an amino group on a primary carbon atom, only processes k_Δ and k_s(c) compete.[43,44]

The view of Collins is disproved most convincingly in those cases where comparative data on deamination and solvolysis are available. Since the increase in demand for participation on going from solvolysis to deamination occurs in $S_\Delta 1$ routes of these reactions, model compounds that mainly give rearranged products are of particular interest. The reactions of model tosylates and amines of fenchane and bornane fully satisfy this requirement.[25,26] It is worth considering these results of Hückel et al. in greater detail on the basis of Scheme 13, when it is borne in mind that previously they were of interest to Collins from the point of view of deamination only occurring via classical ions.[42] The latter approach is not able to explain certain facts that can readily be accommodated by the assumption that processes k_Δ and k_s occur at the same time, as is shown in Scheme 15 for deamination of *endo*-fenchylamine (XXXV)‡.

Scheme 15

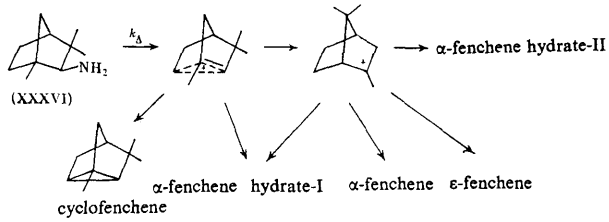


In fact, deamination of *endo*-amine (XXXV) gives in total more than half of the products from displacement of the C(1)−C(7) bond whereas the *exo*-amine (XXXVI) rearranges almost exclusively with

‡ Here and subsequently in Schemes 15–18, products with a content of less than 1% of the reaction mixtures are not given.

migration of the C(1)–C(6) bond (Scheme 16).

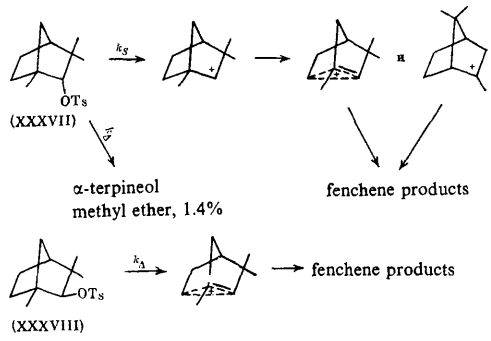
Scheme 16



At the same time, in the solvolysis of the epimeric fenchyl tosylates (XXXVII) and (XXXVIII) such a dependence of the direction of skeletal displacement on the configuration of the leaving group does not occur (Scheme 17). This indicates that deamination of amine (XXXV) occurs to a considerable extent via the k_Δ route involving the C(1)–C(7) bond whereas in solvolysis of the analogous tosylate (XXXVII) there is virtually no participation of this bond. On the basis of Scheme 15 the results of deamination via the k_Δ route conform completely with the stereoelectronic requirements of the nonclassical carbocations (XXXIX) and (XL). This idea, in contrast to the view of Collins, can be used to explain the absence of *exo*-fenchol in the mixture while the yield of *endo*-fenchol is 7%. Similarly, it must be assumed from the isolation of borneol in the absence of isoborneol (the *exo*-epimer) in the mixture that nonclassical carbocation (XXXIX) isomerises to nonclassical carbocation (XL). The interconversion of these carbocations is postulated in the decomposition of the corresponding sulphonyl hydrazones (see the review of Ando[3]).

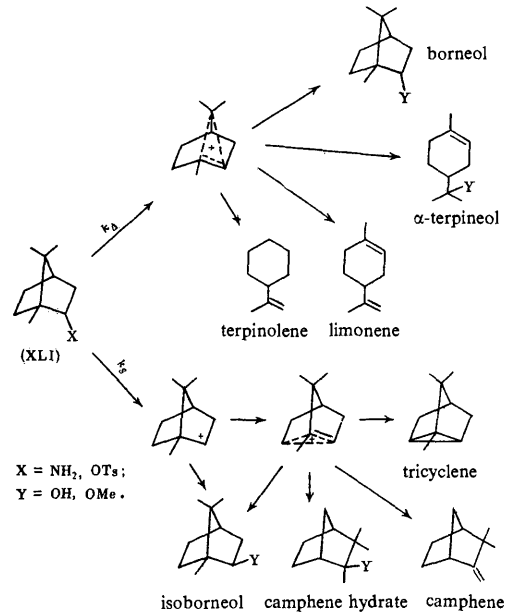
A quantitative determination of the relative contribution of the k_Δ and k_s processes in deamination and solvolysis can be made from Schemes 15–17. The ratio of k_Δ to k_s for the deamination of *endo*-fenchylamine (XXXV) is 1.4:1 in water and zero (in AcOH) or close to this value (in MeOH) for solvolysis reactions of *endo*-fenchyl tosylate (XXXVII). It should be emphasised that the k_Δ and k_s processes are compared exclusively on the basis of the S_Ni mechanism.

Scheme 17



The latter condition is not completely fulfilled for the model bornane compounds (XLI) (Scheme 18). It may be assumed, however, that the contribution of the S_N2-type mechanism k_s(c) is small, on taking into account the small content of inverted bornane products in the resulting mixtures. Assignment of the yields of products from the k_Δ and k_s routes in accordance with Scheme 18 leads to the following ratios of k_Δ to k_s: ~0.7:1 for deamination in water and ~0.005:1 for methanolysis of the tosylate (for quantitative data on the product content, see the studies of Hückel et al.[25,26]).

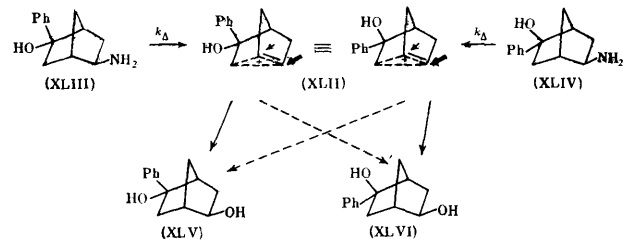
Scheme 18



In a number of alicyclic compounds one of the main arguments of Collins et al. in favour of the intermediate formation of a classical cation is as follows: the nonclassical carbocation (XLII) cannot be a common intermediate species in the reaction of amines (XLIII) and (XLIV) since each of them forms products (XLV) and (XLVI) in different ratios (2.3:1 and 1:1.7 respectively).[18,42] In the opinion of Collins, this fact suggests an equilibrium of classical cations which has not been reached, since solvolysis of the analogous sulphonates with formation of an intermediate nonclassical ion gives the same ratio of products (XLV) and (XLVI).[42]

It should be stated that the above-mentioned tendency of the regioselectivity of nucleophilic attack in deamination[7,8] to change can readily be used to explain this result with the concept of nonclassical ions. In the deamination of amines (XLIII) and (XLIV) the same nonclassical carbocation (XLII) is probably formed, being bonded in different ion pairs, in each case the nucleophile attacks the site of nitrogen elimination with a certain preference. In this connection the predominance of product (XLV) in the deamination of amine (XLIII) becomes clear, as does the predominance of product (XLVI) in the deamination of (XLIV). This is shown in Scheme 19.

Scheme 19



In the studies reviewed, Collins et al. include products whose content in the mixture is extremely small (for example, 0.114% and 0.039%) in their discussion of the mechanism, while the reaction mixtures from deamination are analysed without separating the

alcohol and acetate products.[42] The example given has been discussed since it is a good illustration of the experimental difficulties in the comparative study of solvolysis and deamination, particularly in models of norbornane compounds. An analysis of the experimental data and choice of routes for forming deamination products is often very troublesome not only because of the variety of products obtained but also as a result of possible competing reactions that take place by S_N1 and S_N2 mechanisms.[45] Berson indicates the difficulty of obtaining reproducible results.[22] There are features that are quite often ignored such as the need for a quantitative determination of the epimeric purity of the initial amines and sulphonates, the possibility of the diazonium ion epimerising via a diazoalkane, the occurrence of "internal re-entry" (trapping, Ed. of translation) of the leaving group in solvolysis, the influence of micellar effects in deamination, and the effect of temperature differences when conducting the reactions.[8] These complications to some extent help to answer the question as to why the substantial contribution of processes with anchimeric assistance in deamination often escapes the attention of research workers. Some of these factors are considered below in greater detail.

Thus, in Berson's study[22] discussed above, an analysis of a mixture of only some acetate products of deamination leads to the conclusion that there is a reduction in the degree of σ-participation compared to solvolysis, not in a "pure" S_N1 process but in a combination of S_N1 and S_N2 reaction routes.

Internal re-entry of a sulphonate group can only affect the comparability of results in certain cases. For many purposes titrimetric rate constants (k_t) rather than polarimetric rate constants (k_α) (for optically active sulphonates) can be used, since the error introduced is small; in solvents such as water and trifluoroacetic acid the ratio of the constants $k_\alpha : k_t$ is $\sim 1:1$, in methanol it is 1.2:1, and in aqueous acetone 1.4:1.[46] However, in ethanol (2.94:1) and acetic acid (3.46:1) the difference between k_α and k_t should probably be taken into account. On the whole this factor may result in a "thermodynamic" stereochemistry of the solvolysis products, which quite often imitates the stereochemistry of the k_Δ process. At the same time deamination, which is devoid of internal re-entry of leaving nitrogen, gives a purely "kinetic" product stereochemistry, which as a rule corresponds to competing k_Δ and k_s processes.

A factor such as micellar effects in deamination should be taken into account in a comparative study of the two reactions. It may be concluded from the literature data that the formation of micelles of diazonium ions is typical for relatively stable primary diazonium ions.[47] In this case the change in the stereochemistry of nucleophilic attack on reaching a critical micellar concentration occurs only for superweak nucleophiles such as perchlorate, fluoroborate, tosylate, and camphor sulphonate anions;§ such effects do not occur in "micellar" deamination in the presence of Cl^-, Br^-, and AcO^- anions.[50] In checking the reproducibility of the results it is useful to vary the concentration of the initial amine. Thus, in one study[47] micellar effects of primary diazonium ions occurred when the concentration was changed approximately by a factor of three.

The effect of temperature changes on the comparability of the results of solvolysis and deamination should also be considered. Usually deamination is carried out at temperatures close to room temperature while solvolysis occurs at an appreciable rate at higher temperatures, and the difference can reach 100 °C or more. In this connection the results of direct measurement of the rate constants of the k_Δ and k_s processes in the acetolysis of β-arylethyl tosylates at different temperatures[51] are of interest. The ratio of k_Δ/k_s for the model tosylates (XLVII)–(XLIX) changes symbatically (nonlinearly) with temperature, the increase in temperature always involving a more rapid increase in k_Δ (Fig. 1). For the acetolysis of 2-phenylethyl tosylate (XLVII) extrapolation of the linear dependence of log (k_Δ/k_s) on $1/T$ to room temperature gives a lower value of the ratio of k_Δ/k_s ($\sim 0.6:1$) compared to that calculated for the deamination of 2-phenylethylamine (L) in AcOH at room temperature ($\sim 0.8:1$).[52] Despite the proximity of the extrapolation made by us, it can be qualitatively maintained from this result that the increase in the contribution of the k_Δ process in deamination compared to solvolysis does not result from the different temperature conditions for carrying out the reactions. On the other hand, the higher temperature of solvolysis levels out the differences in the ratios of k_Δ/k_s due to the properties of the leaving groups. This is probably related to a deterioration in solvation conditions of carbocations when the temperature is increased. It cannot be excluded that the S_N2-type k_s(c) processes in solvolysis are suppressed, since this mechanism requires a strict orientation of the nucleophile. Thus, the phenomenon of "temperature levelling" indirectly confirms the concept that the increase in demand for participation may be due to insufficient external solvation. It follows from the results discussed that this property of nitrogen as a leaving group may remain unnoticed in a comparative study of solvolysis and deamination if the temperature conditions for conducting the reactions differ sufficiently strongly.

IV. The Hammond postulate and Curtin–Hammett principle applied to a comparative study of deamination and solvolysis

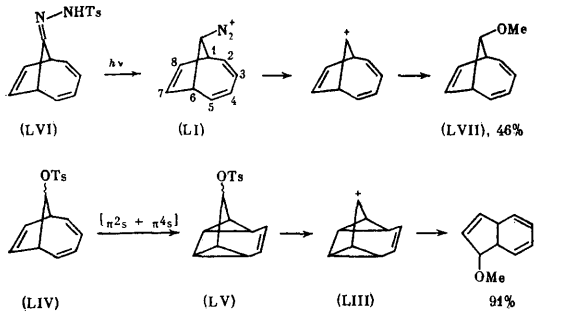
As a result of the widespread propagation of ideas about the obviously classical nature of carbocations in deamination reactions there have been attempts to use such reactions as a model for a typical process that has an "early" transition state. Extracts from many studies, including comparatively recent ones, can be quoted. For example: "deamination ... occurs with formation of an energy-rich diazonium ion, which makes the transition state of its decomposition 'early', i.e., without any change in nuclear coordinates (vertical ionisation). As a result of this, deamination may produce cations with an undistorted geometry that are not formed in solvolysis; the latter lead directly to more stable bridged forms."[3]

Another example is: "...solvolysis and deamination give a fundamentally different result. Solvolysis with its 'late' transition state on the reaction coordinate assists the transposition of the atomic nuclei in such a manner that the route is attained with the minimum of energy. On the other hand, deamination, which starts with an energy-rich diazonium ion passes through its transition state 'earlier' and without any significant distortion of the positions of the nuclei."[53] At first glance, the latter conclusion follows on logically from the stereochemical result shown in Scheme 20. The essential difference between solvolysis and deamination of compounds with the same skeleton is identified by Kirmse as the significant example

§ For example, this important phenomenon as well as the possibility of reactions occurring by an S_N2 mechanism has not been taken into account in studies[48,49] on the deamination of alkylamines in the presence of superweak nucleophiles.

of the formation of a "free carbocation" during decomposition of a diazonium ion.[5]

Scheme 20



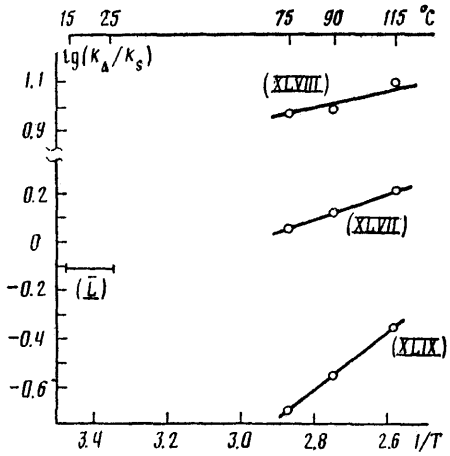
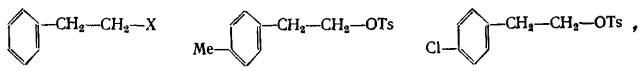
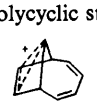


Figure 1. Dependence of the ratio of log (k_Δ/k_s) on temperature in the solvolysis of tosylates (XLVII)–(XLIX) from the data of Jones and Coce[51] and the ratio of log (k_Δ/k_s), calculated from the results of Coce,[52] in the deamination of amine (L) at room temperature; the ratio of k_Δ/k_s was obtained with the following assumptions: 1-phenylethanol (yield 18%) is formed by route $k_s(S_Ni)$; the proportion of k_Δ in the formation of 2-phenylethanol (yield 82%) is approximately equal to double the percentage of migration of the label: $k_\Delta/k_s \sim 44/(38 + 18)$;



(XLVII) X = OTs, (L) X = NH_2. (XLVIII) (XLIX)

Meanwhile, an essentially different interpretation of Kirmse's results[53] is possible. The diazonium ion (LI) decomposes by the k_Δ route with anchimeric assistance from the C(7)–C(8) bond, giving the nonclassical carbocation (LII), whereas solvolysis occurs via the classical cation (LIII) (k_s), which is stabilised through the formation of a polycyclic structure.[8]



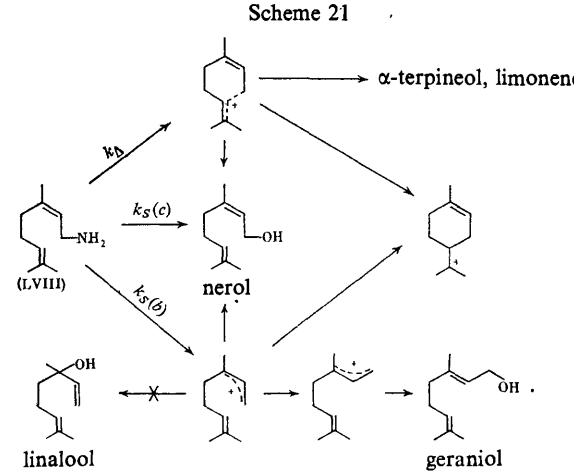
(LII)

In fact, from the equal rates of solvolysis of epimeric tosylates (LIV) and the lack of dependence of the composition of the reaction mixture on the configuration of the sulphonate group and the nature of the solvent, Kirmse and Voigt[53] correctly assume that the rate-limiting stage of solvolysis is formation of the intermediate tosylates (LV). However, no account was later taken of the essential characteristic that the formation of a similar polycyclic structure during the photochemical reaction of tosyl hydrazone (LVI) is prevented by orbital symmetry. An intramolecular Diels–Alder reaction in the rigid bicyclo[4.2.1]nona-2,4,7-triene system permits only a supra-suprasurface cycloaddition involving six electrons [$\pi 2_s + \pi 4_s$], which is photochemically forbidden. Consequently, stabilisation of the cation site during photochemical deamination cannot occur in the same way as in thermal solvolysis, and it probably occurs by intramolecular participation of the C(7)–C(8) bond to form ion (LII), which is suggested by the formation of only one of the two possible epimeric products (LVII).

The study by Bunton et al.[54] concerning a comparative deamination of nerylamine (LVIII) and solvolysis of the phosphate and chloride with the same skeleton is a similar example. The application of Scheme 13 from Section II to nerylamine gives Scheme 21, in which the k_Δ and k_s routes cannot be separated quantitatively. Nevertheless, Bunton et al.,[54] by indicating the relatively lower yield of cyclisation products in deamination, conclude that π-participation is considerable in the formation of the transition state for neryl chloride and neryl phosphate whereas elimination of nitrogen from the diazonium ion does not require neighbouring-group assistance.

The following features of this deamination reaction should be mentioned. Firstly, the total yield of identified products is low but the relative proportion of cyclisation products is almost the same as in solvolysis. Secondly, in deamination there is virtually no linalool formed, which again supports the idea of a change in regioselectivity in this reaction and also indirectly suggests a lower contribution of the k_s(b) process, since solvolysis gives 20–25% linalool against 9–14% geraniol in deamination. However, on the whole, a conclusion about the quantitative ratio of the k_Δ to k_s processes cannot be made using this model compound, as is evident from Scheme 21. Nevertheless, the results discussed by Bunton et al.[54] are used to illustrate the applicability of the Hammond postulate.

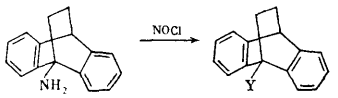
Scheme 21



The account of the different versions of the theory of an "early" transition state in deamination could be continued. However, the material presented in the previous sections suggests the reverse:

participation probably starts at the early stages of nitrogen elimination and the transition state is thus structurally similar to the final nonclassical carbocation. How can this conclusion be made to fit the generally accepted idea about the high exothermicity of this fundamental stage?

In fact, the exothermicity of nitrogen elimination from a diazonium ion is not in doubt in the majority of cases. Nitrogen is known to be eliminated with ease even from bridgehead positions. For example, amine (LIX) undergoes 47% reaction after 15 s at −70 °C, which is virtually impossible for traditional leaving groups ($\Delta\Delta F \geqslant 20$ kcal mol^{-1}).[55]



(LIX)

Y = Cl, OEt.

There have been various determinations of the height of the activation barrier and the heat of reaction for decomposition of an alkyldiazonium ion. Corey et al.[21] determined the heat of reaction from the sum of the ionisation potential of the sec-alkyl radical (8 eV), the energy of homolytic dissociation of the $C-N_2^+$ bond (4 eV), and the first ionisation potential of the nitrogen molecule (−15.6 eV). The value of −3.6 eV per mol obtained for ΔH is 83 kcal, which is quite unsuitable even for an approximate determination of the height of the activation barrier. This barrier is probably not as small as may be suggested from general considerations.

Direct kinetic measurements for stable diazonium ions give values in the region 10−20 kcal mol^{-1}. Thus, the energy of activation for elimination of nitrogen from diazonium ion (LX) is 19 ± 4 kcal mol^{-1}.

$$(CF_3)_2CN_2 + FSO_3H \xrightarrow{-70\ ^\circ C} \underset{(LX)}{(CF_3)_2CHN_2^+} + OSO_2F^-.$$

The very fact of the direct detection of diazonium ions (LXI)[57] and (LXII)[58] suggests that there is a perceptible activation barrier for their decomposition.

$$\underset{(LXI)}{CF_3CH_2N_2^+}\ OSO_2F^-, \quad \underset{(LXII)}{CH_3N_2^+}\ OSO_2F^-.$$

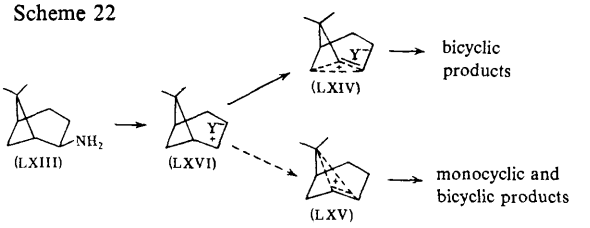
It should be mentioned here that the structure of ions (LX)−(LXII) and the conditions under which they occur (the medium) are not conducive for the elimination of nitrogen by a "pure" S_N1 route, namely, without any external or internal assistance.

A calculation using the MNDO method that was carried out for methyldiazonium and ethyldiazonium ions showed that S_N2 reactions of these ions with different nucleophiles are exothermic processes with a heat of reaction ranging from −16.5 kcal mol^{-1} (reaction of the ethyldiazonium ion with water) to −64.9 kcal mol^{-1} (reaction of the methyldiazonium ion with imidazole). However, decomposition of these same ions by an S_N1 mechanism occurs endothermically (ΔH ranging from +13.9 to +45.8 kcal mol^{-1}), and even when solvation effects are taken into account such endothermicity for the process largely excludes an S_N1 decomposition of ion (LXII).[59]

These results again support the conclusion that nitrogen has no tendency to undergo elimination without external (S_N2) or internal (k_Δ) assistance. The high exothermicity and the low barrier in processes with such assistance together with the reverse situation for the S_N1 route for formation of a classical cation make deamination an "anomalous" process in relation to the extended Hammond postulate.

At first glance the contradiction that arises can be removed by rejecting the idea of anchimeric assistance as such. There is a view that the carbocation is formed without any participation and the cation site is then stabilised by a displacement of the neighbouring group. Thus, in the opinion of Collins, the intermediate carbocations in deamination reactions are classical ions and the subsequent stereoselectivity of the skeletal shifts and nucleophilic attack in an S_N1 reaction are determined by the position of the counterion.[42,60–63] Whittaker has expressed a similar view, according to which participation does nevertheless occur but not in the transition state for formation of a carbocation but at the subsequent stages (Scheme 22).[4,64]

Scheme 22



(LXIII) (LXVI) (LXIV) (LXV)

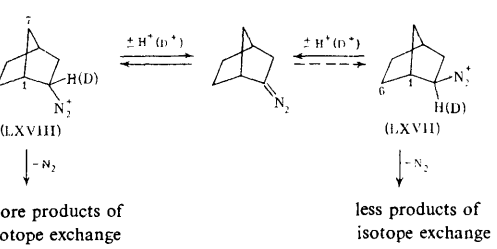
Deamination of amine (LXIII) in AcOH gives only products derived by further reactions of ion (LXIV). In water small quantities of products formed from ion (LXV) occur.

Whittaker proposes that the classical cation (LXVI) is formed at the first stage, the counterion in the intimate ion pair being positioned on the same side as the departing nitrogen. In this case delocalisation of the σ-bond is only possible on the opposite side. In water, separation of the ion pair can partly forestall this type of delocalisation, resulting in the competitive formation of ion (LXV).[4]

Nevertheless, if there is reason to suppose that in this case, as in all the other cases, ions of the type (LXVI) and (LXIV) are formed in parallel rather than successively, this conforms to the general Scheme 13. This is suggested in particular by results that can be used to determine the relative barriers of the decomposition of epimeric diazonium ions.

In the decomposition of the diazonium ions (LXVII) and (LXVIII) in aprotic media, route (d) in the general Scheme 13 starts to play a significant role (Scheme 23). It is worth noting that under these conditions significant deuterium exchange only occurs in the case of the *endo*-substrate (LXVIII).[65]

Scheme 23



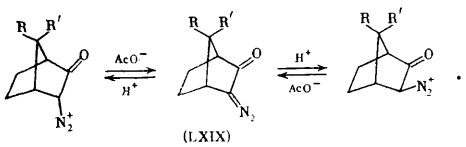
(LXVIII) (LXVII)

Hence there is a higher barrier for elimination of nitrogen for the *endo*-diazonium ion (LXVIII) than for the *exo*-diazonium ion (LXVII). Bearing in mind that participation of the C(1)−C(6) bond is much more effective than participation of the C(1)−C(7) bond, it is doubtful that the difference in the barriers should be assigned to the variable orientation of the counterion. It is more

likely due to participation of the C(1)–C(6) bond in the transition state for elimination of nitrogen from the *exo*-diazonium ion (LXVII).

Fairly recently this proposal received further experimental confirmation in a study of the acid-catalysed decomposition of diazoketones (Scheme 24).[66]

Scheme 24



(LXIX)

	k_{H^+}, mol^{-1} s^{-1}	
	exo	*endo*
R = H, R′ = iso-Pr	7.4	0.47
R = H, R′ = t-Bu	0.28	0.06
R = iso-Pr, R′ = H	55	0.8
R = t-Bu, R′ = H	80	1.2
R = H, R′ = H	—	—

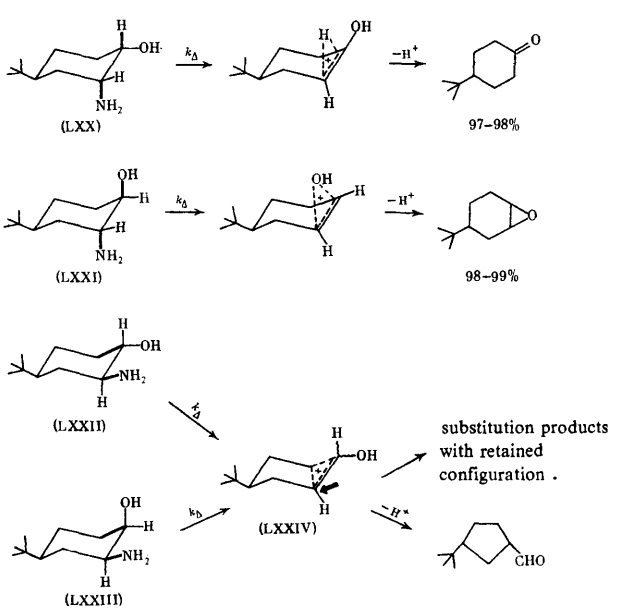
It can be seen from the results in Scheme 24 that the rate constants of reaction for the *exo*- and *endo*-epimers differ by a factor of 10–100. There is reason to suppose that in the presence of acetate anion, elimination of nitrogen in the protonation of diazoketone, is, at least in part, the rate-limiting stage.[66] This is due to the competing deprotonation of the diazonium ions. In a medium without acetate anion added the rate-limiting stage is protonation of diazoketone (but it probably has a similar rate to the nitrogen elimination stage). The enthalpy of activation of this reaction for diazoketone (LXIX), R = H, R′ = iso-Pr, in aqueous acid is 13.7 kcal mol^{-1}, which may be similar to the enthalpy of nitrogen elimination. The entropy of activation (–8.4 e.u.) increases the barrier by a further 2.3 kcal mol^{-1} under normal conditions¶.[66]

The many illustrations of the extended Hammond postulate in the case of deamination are based on an estimate of the energy of activation for decomposition of the diazonium ion in the region of 3 to 5 kcal mol^{-1} that was made by Streitwieser from general considerations.[16,17] The findings reported above confirm that this barrier usually does not exceed 10–15 kcal mol^{-1} when the process is accompanied by internal or external assistance. Thus, the contradiction between the concept of the increase in demand for participation in deamination developed here and the extended Hammond postulate is retained. It may be assumed that in an exothermic reaction with assistance (which in turn gives rise to exothermicity), the "early" substrate-like transition state contains a partial displacement of the neighbouring group in so far as even when the diazonium ion exists there can arise a "low-electron, multicentred" delocalisation involving the electrons of the neighbouring periplanar bond, which is accompanied by a partial rehybridisation of the carbon atom bonded to the charged nitrogen. This specific precarbocation stage of nonclassical delocalisation in the diazonium ion does not contradict the existing facts. It may be confirmed or disproved using quantum-chemical methods, but these results have so far not appeared in the literature.

In our opinion, regardless of whether it is possible at the present time to resolve the contradiction between the Hammond postulate and the hypothesis developed here, the predictive potentialities of the latter should be utilised. It is useful to give as an example the solution of the problem relating to the reactions of diastereomeric cyclohexylamines whose conformations are stabilised by the introduction of bulky alkyl substituents.

Thus, in terms of the general Scheme 13, deamination of the diastereomeric amines (LXX)–(LXXIII) is given by Scheme 25, in which the determining factor is participation of one of the periplanar neighbouring bonds. Moreover, by using Scheme 25 it is possible to answer the question raised previously, but up to now not having received a satisfactory explanation (see the reviews of Kirmse[2] and Moss[11] and the references in them), namely: why do axial cyclohexylamines of the type (LXX) and (LXXI) give many elimination products and only a few equatorial (inverted) products while equatorial amines of the type (LXXII) and (LXXIII) mainly form substitution products with retained configuration and few elimination products?

Scheme 25



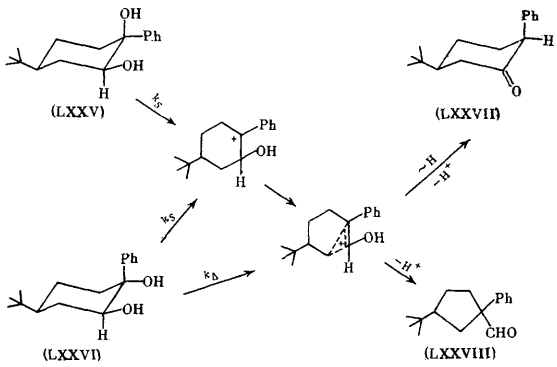
It can be seen from Scheme 25 that in the typical axial amine (LXX) participation of the C–H bond must be less effective than participation of the C–C bond of the ring in any equatorial epimer. The latter, for its part, gives nonclassical cations of the type (LXXIV), whose stereoelectronic requirements assist the formation of substitution products with retained configuration.

¶If it is assumed that the kinetic parameters for protonation of diazoketones are similar to those for the nitrogen elimination stage, the results of Kronis et al.[66] do not support the idea of the entropy factor, when there is a low enthalpy of activation, having a decisive effect in deamination.[4,67,68] According to this hypothesis the entropy factor inhibits the formation of a nonclassical carbocation as a more ordered species under conditions where the solvate shell has little effect on the degree of ordering of the transition stage. It is evident from the activation parameters stated above that the entropy contribution is not decisive.

In the meantime the lesser requirement for ordering of the solvation shell from a nonclassical cation compared to a classical cation[69] may in fact make the nonclassical cation "entropy-preferred". Thus, according to the results of two studies,[70,71] diazoalkane (LXIX), R = R′ = H, after being protonated decomposes with σ-participation.

As expected, glycols (LXXV) and (LXXVI), which are analogous in structure to the amino alcohols (LXX)–(LXXIII), do not react stereospecifically. The products—(LXXVII) and (LXXVIII)—are formed in the ratio 9 : 1 whatever the configuration of the leaving group[2,72] (Scheme 26).

Scheme 26



In this case it is worth comparing the reactions of aliphatic and alicyclic substrates. Thus, the example shown in Scheme 25 is similar to the pinacolic deamination discussed earlier (Scheme 12). In both cases the result contradicts the Curtin–Hammett principle in that the ratio of products formed from the different conformations (or diastereomers) of the substrate depends on the relative populations of the conformations (or on the configuration of the leaving group).

There is reason to suppose that the above-mentioned "violations" of the extended Hammond postulate and Curtin–Hammett principle in deamination have a common origin which should be looked for under the specific conditions of ionisation of the substrate. These conditions, which have been discussed in detail in the preceding sections, lead to the formation from different conformers (diastereomers) of different carbocations (as a rule, nonclassical) that tend not to undergo interconversions. As has already been mentioned, one of the causes may be a specific precarbocation ionisation stage which involves a partly "nonclassical" diazonium ion. Under these conditions formation of carbocations from diazonium ions is kinetically controlled and the stereospecificity is not disturbed.

In solvolysis, where anchimeric assistance in the S_N1 process plays a lesser role but internal re-entry plays an important part†, the composition of the intermediates is to a greater degree thermodynamically controlled. The Curtin–Hammett principle is fulfilled precisely in the "thermodynamic" region of nucleophilic substitution, which is accessible to only a limited degree for nitrogen elimination reactions (see, for example, Scheme 14). However, this fact makes deamination a convenient method for carrying out uncommon (such as the Dem'yanov rearrangement) and directed skeletal rearrangements.

† There is no information about internal re-entry of nitrogen in the decomposition of a diazonium ion in aliphatic compounds. It may be judged that this is a very insignificant process from the results on the insertion of nitrogen into the reactive phenyl cation; at 300 atm 2.46 ± 0.4% external nitrogen is inserted.[73]

On the other hand, decomposition of a diazonium ion is a single-stage fundamental process and it conforms to the Hammond postulate. In this sense the diazonium ion must also be partially stabilised through nonclassical delocalisation.

Having summarised the results of the critical examination of the literature conducted above, we consider it desirable to note the following fundamental characteristics of deamination reactions as compared to solvolysis.

1. The formation of a charged diazonium ion species at a precarbocation stage helps to develop a greater degree of anchimeric assistance in deamination as compared to traditional solvolysis. By using deamination it is possible to carry out purposefully rearrangements which are impossible or difficult in other reactions. In this case the group periplanar to the leaving nitrogen is always displaced. In a number of cases replacement of a separating sulphonate group by nitrogen is equivalent to conducting solvolysis in a much more ionising and less nucleophilic solvent.

2. The direction of nucleophilic attack in S_N1-deamination should be expected to correspond to the stereoelectronic requirements of the nonclassical carbocation in which participation of the neighbouring periplanar group develops. Regioselectivity must be taken into account; substitution occurs primarily on the site of nitrogen elimination.

3. In a comparative study of deamination and solvolysis, particular factors that affect the comparability of the stereochemical results of the two reactions must be taken into account:

a) the possibility of partial epimerisation of a diazonium ion via a diazoalkane;

b) internal re-entry of the leaving group in solvolysis;

c) micellar effects in deamination;

d) the difference in the temperature conditions for carrying out the reactions;

e) the necessity of making a separate analysis of deamination products that belong to different classes of compounds.

4. The observed variance of the stereochemistry of deamination products with the extended Hammond postulate and Curtin–Hammett principle probably has a common origin and can be accounted for in a similar way. The concept of nonclassical delocalisation of the positive charge in a diazonium ion itself may serve as one of the explanations.

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Structural features and reactivity of tetrahalomethanes

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ABSTRACT. It is shown from an analysis of data on the structure and properties of tetrahalomethanes CX_4, where X = Cl, Br, I, that their chemical behaviour in many respects depends on the energy accessibility of the lowest unoccupied molecular orbital, which is the antibonding analogue of a bonding orbital of σ-type. This characteristic is responsible for, on the one hand, the occurrence of intramolecular interactions between halogen atoms and, on the other hand, their electrophilic properties in reactions with electron donors.

The bibliography includes 183 references.

Contents

I. Introduction 193
II. Structural features of polyhalomethanes 193
III. Reactions of tetrahalomethanes with free radicals 196
IV. Reactions with charged nucleophiles 197
V. Reactions with electron-neutral nucleophiles 198

I. Introduction

The problem of nucleophilic substitution in alkyl halides is one of the most frequently studied in theoretical organic chemistry. Up to the present time the structural factors that determine the reactivity of the substrate and nucleophile are generally apparent, the stereochemical characteristics of these processes are clear, and there exists the possibility of controlling a reaction using the solvent.[1,2] However, it has been observed for a long time that as the degree of halogenation of CH_nX_{4-n} molecules increases, the rate of reaction of bimolecular nucleophilic substitution usually decreases despite the increase in electron-withdrawing action of the substituents. Tetrahalomethane molecules, which are the limiting case of this type of α-substitution, react very sluggishly with nucleophiles. The reactions only take place under much more severe conditions and their results are ambiguous.[3] The nature of this type of α-effect is not at all clear up to the present time. Different explanations of this phenomenon have been put forward both in terms of the valence bond approach[4] and the molecular orbital approach.[5–7]

In recent times tetrahalomethanes, principally carbon tetrachloride and carbon tetrabromide, have started to be used effectively in different syntheses, especially those involving phosphorus-containing nucleophiles,[8] to give products whose formation cannot be accounted for on the basis of substitution reactions on the carbon atom.

Recently the concept of so-called "X-philic reactions" was developed.[9] It accounts for this and other similar reactions that take place by attacking a peripheral site rather than the central carbon atom on the basis of the theory of the perturbation of molecular orbitals. Ligand transfer to the nucleophile results from such reactions. By solving this problem in a general form and not solely for halogen-containing substrates, the authors who developed this concept did not set themselves the task of trying to find the structural causes through which a tetrahalomethane becomes the source of a "positive" halogen. Moreover, being clearly aware of the possibility of an alternative to the mechanism of an X-philic reaction, they confined their study solely to a theoretical approach. Meanwhile, there is a variety of information on the use of carbon tetrahalides in different chemical reactions related to halogenation of a nucleophile, in which the existence of radical intermediates have been recorded. The lack of correspondence that occurs, in our opinion, can be resolved by establishing the structural features and reactivity of polyhalomethanes from the available information, which, despite its considerable volume, has not been correlated to date. What has been stated above, together with the possibility of the future use of the conclusions obtained to interpret similar reactions of tetrahalides of other elements such as phosphorus,[10] constituted the reason for writing this review.

II. Structural features of polyhalomethanes

The properties of polyhalomethanes are determined in many respects by the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO).

According to nonempirical calculations the electronic configuration of tetrahalomethanes can be represented by the following MO sequence:[11,12]

$$(1a_1)^2\,(1t_2)^6\,(2a_1)^2\,(2t_2)^6\,(1e)^4\,(3t_2)^6\,(1t_1)^6\,(3a_1)^0\,(4t_2)^0.$$

The orbitals with e, $3t_2$, and t_1 symmetry are classed as π-type group orbitals formed from the p_z and p_y atomic orbitals (AO) of the unshared electron pairs (UEP) of the halogen atom. The $3a_1$ and $4t_2$ orbitals are classed as antibonding analogues of the $2a_1$ and $2t_2$ σ-type bonding orbitals.

Localisation of the upper occupied levels and their composition have been demonstrated by X-ray and photoelectron spectra, a detailed discussion of which is conducted in a recently published monograph.[13] In this case the first ionisation potential (IP) of halomethanes can be related to the HOMO energy, and the energy of the LUMO can be obtained by comparing these values and the energies of the $p \rightarrow \sigma^*$ transitions in UV spectra,[14,15] which generally correspond to the difference in energy between HOMO and LUMO.

In contrast to alkyl fluorides CH_nF_{4-n}, in which the energy levels of the UEP of the fluorine atoms lie below the bonding energy levels of the σ bonds, which are most apparent in the far UV region,[15] their analogues with heavier halogen atoms have certain characteristics.

Thus, the first IP in these derivatives correspond to the UEP of the halogen. It is clear that on increasing the degree of halogenation and also on replacing Cl by Br, the magnitudes of the first IP decrease (Table 1), which is probably due to a decrease in orbital energy of the ligand atoms on changing from Cl to Br and a decrease in effective charge on the carbon atom.[13]

Table 1. First ionisation potentials (IP, eV) and energies of the $p \rightarrow \sigma^*$ transition (E, eV) for halomethanes.[13,14]

Compound	F		Cl		Br		I	
	IP	E	IP	E	IP	E	IP	E
CH_3X	13.1	—	11.29	7.3	10.54	6.20	9.54	4.77
CH_2X_2	11.29	—	11.10	7.29	10.61	5.64	9.52	—
CHX_3	14.28	—	11.48	7.09	10.47	5.10	9.21	—
CX_4	16.30	—	11.69	7.08	10.39	4.90	9.10	3.20

When the energies of the $p \rightarrow \sigma^*$ transitions in the UV spectra of alkyl halides CH_nX_{4-n}, X = Cl, Br, I, n = 0–3 are examined and compared with the ionisation potentials, it can be seen that the energy gap between the HOMO and LUMO in this series of compounds decreases since the energy of the LUMO successively decreases on replacing chlorine with bromine and iodine and by increasing the degree of halogenation of methane.[16] These changes in the HOMO and LUMO should apparently assist both intra- and intermolecular interactions which depend on the energy of the frontier orbitals. For example, as the degree of halogenation of methane increases, the electron affinity should increase.[17] This conclusion is supported by the decrease in the values of the half-wave potential of polarographic reduction on increasing the number of bromine atoms in a methane molecule,[18] since it is known that its value is proportional to the energy of the LUMO.[19] This is also convincingly shown by the spectroscopic data of dissociative attachment of electrons to halomethane molecules.[20–23] The results obtained by different authors suggest that when an electron interacts with a halomethane molecule it is placed in its σ^* orbital with t_2 symmetry to form a temporary anionic state. This is very unstable and decomposes almost immediately. A quantum-chemical calculation with a CNDO/2 approximation on an *sp* and *spd* basis was used to analyse the different ways for the decomposition of such CX_4^- intermediates when X = Cl, Br, I:[24]

$$CX_4^- \rightarrow CX_4 + e^-, \quad CX_4^- \rightarrow CX_3^- + X^\cdot, \quad CX_4^- \rightarrow CX_3^\cdot + X^-.$$

It transpired that the route leading to a halogen anion and trihalomethane radical has the least energy. Consequently, this route is predominant in the dissociative attachment of an electron. In this case the maximum yield of halogen will occur at the absorption energy of the electron. It is possible thus to determine the electron affinity in CH_nX_{4-n} molecules, which increases as the number of halogen atoms increases and on going from chloromethanes to their bromine analogues,[22,23] which accords with the direction of change in energy of the LUMO in these molecules.

The steric structure of halomethanes with a varying degree of substitution has been studied in detail in both the gas phase and crystalline state. Extensive tables of data on interatomic distances are available in a monograph[25] and booklets.[26,27] Data obtained by the same or comparable methods are given in Table 2.

Table 2. Carbon–halogen bond lengths in CH_nX_{4-n} molecules, Å.[25–27]

Compound	F		Cl		Br		I	
	g	c	g	c	g	c	g	c
CH_3X	1.383	—	1.781	1.805	1.939	1.863	2.133	2.134
CH_2X_2	1.357	—	1.767	1.768	1.925	1.91	—	2.12
CHX_3	1.332	—	1.758	1.750	1.930	—	2.12	2.18
CX_4	1.319	—	1.767	1.751	1.942	—	2.18	—

Note: g—gas phase; c—crystalline state.

Despite the fact that the absolute values of the C–X interatomic distances obtained for the different phase states are not the same, their patterns of change with a successive build-up of halogen atoms as well as when changing the nature of the halogen atom are clearly visible. On the one hand, there is an evident tendency of the C–X bond length to decrease with an increase in the number of halogen atoms in halomethanes in the case of the relatively compact fluorine and chlorine atoms. This can be followed most clearly in fluoromethanes. This would appear to result from the increase in effective electronegativity of the carbon-centred fragment, so that there is a reduction in polarity of the bond and as a result a reduction of the interatomic distance.[28] This is also indicated by the decrease in dipole moment of the C–X bond as the degree of halogenation of methane increases[29] and also by the occurrence of the shortest recorded carbon–halogen bond in the case of tetrahedral chlorides and bromides in chloro- and bromotrinitromethanes (1.712 and 1.885 Å respectively).[25]

On the other hand, on going to the more diffuse, bulky bromine and iodine atoms a tendency for the C–X bond to lengthen becomes apparent. This effect may be due to the steric interactions of the neighbouring halogen atoms, which is suggested, for instance, by the unusual intramolecular distances of X...X in the dihalomethanes CH_2Br_2 and CH_2I_2 [30,31] and in CCl_4.[32] In these molecules they are noticeably less than the sum of the van der Waals radii of the halogen atoms. It is also thought that these interactions reduce the energy of dissociation of the C–X bond, where X = Cl, Br, I, as the methane is halogenated, which does not occur for fluorination. It is possible that for this reason the valence force constants of this bond are reduced.[34]

It appears that the interactions of the geminal halogen atoms also have an effect on the enthalpy of formation of halomethanes. It has been observed that when there is a build-up of halogen atoms, this function increases nonlinearly.[37]

Another interesting feature of these alkyl halides CH_nX_{4-n}, X = Cl, Br, I, is the effect of the decrease in halogen–halogen intermolecular distances in the crystalline state.[30,31] It is thought

that this occurs as a result of charge transfer from a halogen atom to the σ^* orbital of a C–X bond in neighbouring molecules. This results in a decrease in the magnitude of halogen-halogen intermolecular contacts and consequently to underestimated values of the van der Waals radii.[38,39] It is therefore thought that the very concept of a radius for halogens is only significant when applied to contacts with atoms that do not have unshared electron pairs.

Table 3. Dissociation energy of the C–X bond in halomethanes CH_nX_{4-n}.[35,36]

Compound	Dissociation energy, kcal mol^{-1}			
	F	Cl	Br	I
CH_3X	112	83.6	69.7±1	54
CH_2X_2	114.5	81±3	62.7±5	45.5
CHX_3	128±5	77.2±5	56.7±5	37
CX_4	92.0±4	73.3±2	49.7±5	28.5

It cannot be excluded that this intermolecular charge transfer has an effect on the length of the C–X bond in tetrahalomethanes that is determined in the crystalline state. It should also be mentioned that a similar but solely intramolecular interaction is quite likely to occur between geminal halogen atoms, making it possible for them to converge to distances less than the sum of the van der Waals radii.

Table 4. Dipole moments of CH_nX_{4-n} molecules (μ), the C–X bond (μ_{C-X}), and the charges on the halogen atom (q_X).[40–42]

Compound	F			Cl			Br		
	μ, D	μ_{C-X}, D	q_X, e	μ, D	μ_{C-X}, D	q_X, e	μ, D	μ_{C-X}, D	q_X, e
CH_3X	1.87	—	0.2083	1.861	1.59	0.0850	1.86	1.52	0.0237
CH_2X_2	1.96	—	0.1983	1.57	1.05	0.0738	1.42	1.03	0.0176
CHX_3	1.62	—	0.1967	1.01	0.55	0.0659	0.99	0.54	0.0190
CH_4	0	—	0.1980	0	0.08	0.0664	0	0.05	0.0208

An increase in the effective electronegativity of the CR_3 fragment in an R_3C-X molecule on increasing the degree of methane halogenation should lead to a reduction in negative charge on the halogen atom through its transfer to the bond. A consequence of this should be a reduction in dipole moment of the C–X bond, as has been mentioned above. In fact, a comparison of the dipole moment of halomethane molecules (the dipole moments are determined in the gas phase in order to exclude intermolecular interactions) with the value of the group dipole moment of the C–X bond [40,41] and the magnitude of the charge on the halogen atom (obtained by calculation using the modified CNDO/2 method[42]) supports this conclusion (Table 4).

The electric polarisability of the molecules may serve as a qualitative measure of the mobility of the electrons and hence may also reflect the intramolecular interactions. In this case the anisotropy of bond polarisability calculated from the molecular anisotropy and the Kerr constants serves as a specific test for such effects.[43,44] For example, in a determination of the ellipsoids of polarisability for molecules of the type CH_2X_2, X = Cl, Br, I, for all three axes and when comparing the results with monohalogen derivatives, it was concluded that the significant experimental deviations from additivity in dihalomethanes are due to the interaction of the neighbouring C–X bonds through space.[45] Since the values of polarisability of the valence MOs decrease with an increase in the number of halogen atoms,[46] it may be assumed that the main contribution to polarisability is provided by the UEP of the halogen atom.

Table 5. Chemical shifts (δ, ppm) of ^1H, ^{13}C, ^{19}F, and ^{35}Cl atoms in halomethane molecules.

Compound	F			Cl			Br		I	
	δ^1H	$\delta^{13}C$	$\delta^{19}F$	δ^1H	$\delta^{13}C$	$\delta^{35}Cl$	δ^1H	$\delta^{13}C$	δ^1H	$\delta^{13}C$
CH_3X	7.1	75.5	271.9	7.1	25.1	40	7.3	10.2	7.6	−23.5
CH_2X_2	8.8	112.2	143.4	9.9	54.2	230	10.1	21.6	9.8	−61.1
CHX_3	10.3	118.8	78.6	11.8	77.7	410	12.4	12.3	6.5	−139.7
CX_4	—	119.9	63.3	—	96.7	560	—	−28.5	—	−229.1

Note. Chemical shifts of the ^1H atoms were measured relative to methane,[47] ^{13}C atoms relative to tetramethylsilane,[48,53] ^{19}F atoms relative to fluorotrichloromethane,[49] and ^{35}Cl atoms relative to an aqueous solution of sodium chloride.[50]

Haloalkanes have been studied repeatedly using radiospectroscopic methods and almost always the relationship between the changes in the spectroscopic characteristics of the indicator atom and the number of halogen atoms on the carbon atom has been investigated. As a rule a build-up of electronegative geminal substituents on carbon in halomethanes results in nonadditive effects which distort the dependences of the spectroscopic properties of these compounds on the structure. The chemical shifts in the spectra of halomethanes in relation to the number and nature of the halogen atoms can be given as such an example (Table 5).

It is clear from Table 5 that with an increase in the number of halogens the ^1H chemical shift is displaced downfield. This type of deshielding conforms to the increased electronegativity of the halomethyl residue and is likely to correspond to a reduction in electron density on the hydrogen atoms. However, it is noticeable that the contribution of a halogen in shielding the proton is not additive, as is indicated, for example, by the unsatisfactory value of the ^1H chemical shift in haloforms using Shoolery constants.[51]

A study of intramolecular interactions in halomethanes using ^{13}C NMR spectroscopy has been undertaken by different authors.[48,52–55]

By treating the chemical shifts of the ^{13}C nuclei in these compounds as the sum of mono-, di-, and tri-atomic increments that take into account interactions along the C–X bond as well as those through space,[48,52] it was possible to make quite an accurate prediction of their value. However, in considering this approach limited, Dostovalova et al.[54] gave greater consideration to the reasons for the nonoadditivity of the changes in this spectroscopic parameter and made an attempt to represent it through the bond increments $\Delta\delta_{C-X}$.[55] These values occur as the ratio of the difference between the chemical shifts of the halohydrocarbon in question and unsubstituted methane to the degree of substitution. The nonlinear change in these values is due to nonbonded interactions between the geminal halogen atoms, which lead to a distortion of their electron shell and consequently to an alteration in the charge on the C–X bond. The nature of such nonbonded interactions is probably similar to that which has been put forward to explain the changes in chemical shifts of ^{13}C and ^{19}F atoms in a number of substituted fluorochloromethanes.[56] In this case overlap of the UEP orbitals of the halogen with the virtual orbitals of the neighbouring carbon–halogen bond is thought to be most likely. This approach is confirmed by quantum-chemical calculations with the CNDO/2 approximation and by the good correlation of the ^{13}C chemical shift with the charge on this atom.

In the opinion of Cheremischin and Schastnev,[57] another reason for the nonadditive changes in chemical shifts of carbon that increase as the number of substituents in halomethanes increases is the occurrence of spin-orbit interaction. It has been observed that this effect is small for chloro derivatives but is substantial for the bromine- and iodine-containing analogues.

NMR spectroscopy of halogen nuclei has, with the exception of fluorine, not been used much for the study of halomethanes.[50,58] This is mainly because of the limitations arising as a result of broadening of the resonance line. Thus, for example, in the ^{35}Cl NMR spectrum of CCl_4 its width is equal to 15 kHz. Nevertheless it can be seen that the stepwise change from methyl chloride to carbon tetrachloride leads to deshielding of the nucleus of the chlorine atom.[50] The linear relationship between the chemical shifts of the ^{35}Cl and ^{19}F atoms indicates that there is a uniform structural effect on the shielding of both nuclei.[58]

An interpretation of the spectroscopic data of nuclear quadrupole resonance (NQR) of the nuclei of halogen atoms using the Townes–Dailey approximation can be used to determine the spatial distribution of electron density around these nuclei, and it has therefore been widely used to study organohalogen compounds, in particular halomethanes.[59]

It can be observed here that as the number of halogen atoms in the methane molecule increases, the NQR frequencies increase, which is interpreted as a consequence of the decrease in ionic nature of the C–X bond. However, it can be seen that the change in frequency is nonadditive.[60]

Introduction of substituents that are electron-donating relative to the halogen into the CX_4 molecule reduces the frequency of ^{35}Cl NQR, while electron-withdrawing substituents increase it. However, the change in frequencies in this case is determined by the inductive effect only to a first approximation. For example, for RCH_2Cl derivatives in which substituent R has unshared electron pairs (X = RO, F, Cl, Br) there are appreciable deviations from a linear dependence, which is due to conjugation of $p \rightarrow \sigma^*$-type.[61,62]

Thus, a study of intramolecular interactions in polyhalomethanes using radiospectroscopic methods shows that the change in spectroscopic characteristics is subject to the effect of the geminal halogen atoms, which in all probability is due to overlap of the orbitals of the unshared electron pairs of the halogen with the low-energy antibonding orbital of the neighbouring C–X bond. This effect is likely to determine the overall specific nature of intramolecular interactions in tetrahalomethanes. The energy availability of the antibonding orbitals of the C–X bond enables CX_4 molecules (X = Cl, Br, I) to exhibit electrophilic properties which give rise to reactions with certain types of charged and neutral nucleophiles as well as with free radicals.

III. Reactions of tetrahalomethanes with free radicals

It was noted earlier that when the number of halogen atoms on carbon is increased, the capacity of halomethanes for dissociative attachment of an electron increases. In this case temporary anionic states are formed, readily decomposing in the case of tetrahalides to a trihalomethyl radical and a halogen anion. Acceptance of an electron into an antibonding orbital accounts for the instability of the intermediate, which, however, decreases with an increase in the number of halogen atoms. This is indicated by a quantum-chemical calculation using the MINDO/3 approximation.[63]

Free radicals, as real electron carriers, should also in principle cause a similar dissociation of a halomethane. In fact, elimination reactions of a halogen from polyhalomethanes by the action of free radicals are well known. It has been shown by a large number of experiments that the energy of activation of the chain-transfer reaction

$$R^{\cdot} + CH_nX_{4-n} \rightarrow RX + \dot{C}H_nX_{3-n}$$

decreases as the number of halogen atoms in polyhalomethanes is increased, and when chlorine is replaced by bromine and then by iodine.[64] It should be emphasised here that such reactions are not typical for fluoromethanes.

Studies of a model chain-transfer reaction in the polymerisation of alkenes showed that in the reaction of the hydrocarbon radicals $(CH_3)_2C^{\cdot}R$, where R = PhO, MeCOO, PhS, Ph, with CBr_4, CCl_3Br, and CCl_4, there is electron transfer from the radical to the polyhalomethane. In this case the rate of reaction decreases in the series $CBr_4 > CCl_3Br > CCl_4$.[65]

Free-radical donor properties relative to tetrahalomethanes have been found in the case of the formation of adducts between 2,2,6,6-tetramethylpiperidine *N*-oxide and carbon tetrachloride.[66] At the same time paramagnetic shifts were detected in the ^1H NMR spectra of chlorine-containing molecules without α-hydrogen atoms in the presence of stable nitroxyl radicals. An analysis of the concentration dependence of these shifts showed that in this case weak complexes are formed between the components.[67] Morishima et al.[68,69] also found a downfield shift of the resonance signal in the ^1H and ^{13}C NMR spectra in the reaction of halomethanes with di(t-butyl)nitroxyl. They relate this phenomenon to the formation of short-lived complexes. The linear dependence between the observed contact shift and the half-wave potential of polarographic reduction of halomethanes serves as evidence of the donor-acceptor nature of these interactions involving a σ^*-type LUMO of the halomethanes. This is suggested by the appearance of a new absorption band in the region 310–370 nm in a solution of the same stable radical in carbon tetrachloride. It is thought that for carbon halides containing hydrogen, a complex is formed through hydrogen bonding,[70] while for tetrahalides the acceptance of electron density may only occur via the antibonding orbital of the C–X bond.

IV. Reactions with charged nucleophiles

During the last fifteen years attempts have been made to obtain carbon compounds with a coordination number greater than four. The highest expectations in this area relate to stabilisation of this unusual state by electron-withdrawing substituents. Hence the pentahalocarbonate anion CX_5^- has attracted a considerable amount of attention from research workers. The most promising method of obtaining this is the reaction of carbon tetrachloride or tetrabromide with phosphonium or tetraorganylammonium halides[71] as halide anion donors. Thus, it was possible to obtain complex compounds, but when they were studied by IR and Raman spectroscopy and X-ray diffraction analysis it was shown[72] that in the crystalline state carbon is not pentacoordinate in these compounds. In this case there is the formation of a complex ion in which a halogen anion is surrounded by four tetrahalomethane molecules with coordination via the halogen atoms (the three-membered fragment C—X—X is linear).

The formation of complex compounds with a $Br_3C-Br..Br^-$ fragment can be accounted for using the following two models. On the one hand, it is possible to form a donor-acceptor complex whose existence is achieved through charge transfer from the halogen anion to an antibonding orbital of the C—X bond or using a vacant 3*d* orbital of the halogen in the carbon halide. On the other hand, it may be assumed that because of the high polarisability of the CX_4 molecule, an electrostatic interaction of the type ion—induced dipole can occur.

An analysis of the X-ray diffraction data showed that the X...X distance in these complexes is considerably less than the sum of the van der Waals radii.[72] It was found for complexes of $R_4N^+Hal^-$ (R = Me, Et; Hal = Cl, Br, I) with CX_4 (X = Cl, Br, I) that the X...X distance increases (for a given halomethane) as a function of the halogen anion in the series $Cl^- < Br^- < I^-$, and it increases as a function of the acceptor molecule (for a given anion) in the series $CCl_4 < CBr_4 < CI_4$. The data obtained provide a basis for classing these complexes as donor-acceptor types. In the opinion of Creighton and Thomas,[72] the acceptor orbital in these complexes is a σ^*-type LUMO.

Recently a nonempirical calculation of the structure and stability of pentahalocarbonate anions CX_5^- (X = F, Cl, Br, I) was carried out. The formation energies of the three most probable structures were compared in this case. One of them has D_{3h} symmetry and two have C_{3v} symmetry. They differ in that the incoming anion coordinates either on the side or the top of the CX_4 tetrahedron.[73] It transpired that a pentahalocarbonate anion with a trigonal bipyramidal structure is unstable for any type of halogen. When the symmetry is reduced to C_{3v} the result is that such structures for X = F, whatever the approach of the incoming anion, are energetically unfavourable and the anion is unstable both in the gas phase and crystalline state. However, for X = Cl, Br, I, the coordination of the incoming anion to the halogen atom situated at the top of the tetrahedron always requires 25—45 kJ mol^{-1} less energy than when approach is made to the side, namely, to the carbon atom. In other words, according to the nonempirical quantum-chemical calculation, attack by the halogen anion on to the tetrahalomethane molecule occurs via a halogen atom, which is in complete agreement with the findings of X-ray structural analysis as given above.

The reaction of organometallic compounds (OMCs) with tetrahalomethanes has been studied for quite a long time and a considerable amount of information relating to this has been collected to date.[74] Information about the mechanisms of such reactions can be found in a monograph.[75]

Among OMCs of Group I metals, organolithium compounds are of the greatest interest. At very low temperatures (−115 to −100 °C) and in media with a high solvating capacity, such as in tetrahydrofuran or its mixtures with ether, a reaction that gives an organic halide and trichloromethyllithium readily occurs:[76—78]

$$R—Li + CHalCl_3 \rightarrow R—Hal + CCl_3Li,$$

R = Me, Et, n-Bu, Ph; Hal = Cl, Br, I.

However, when the temperature is increased, the reaction is different. It is frequently used as a source of dihalocarbenes. Thus, when ICF_3 [79] or CBr_2F_2 [80] is reacted with alkyllithium, difluorocarbene is formed and it is stabilised by alkene cyclopropanation. Reaction of methyl- and butyl-lithium under similar conditions with different tetrahalomethanes in the presence of cyclohexene gives dihalonorcarane in about 90% yield.[77] The change in the outcome of the reaction at an increased temperature is usually related to the ease of α-elimination of lithium halide from trihalomethyllithium. In fact, trichloromethyllithium which is obtained at a low temperature decomposes by 50% over a period of 30 min even at −65 °C according to the scheme

$$CCl_3Li \rightarrow LiCl + :CCl_2.$$

It should be mentioned here that there is no sign of a Wurtz type of condensation in these reactions.[74]

Among OMCs of Group II elements, organomagnesium compounds should first of all be mentioned. As a rule Grignard reagents react with CX_4 in different ways, in the case of alkylmagnesium halides forming complex mixtures of alkanes and olefins. However, it is thought that at low temperatures the reaction takes place via the formation of an organic halide and a trihalomethyl derivative of the metal.[81,82]

Comparatively recently a more detailed study of the reactions of organomagnesium compounds with tetrahalomethanes was made.[83—85] In this case chemically induced polarisation of ^1H nuclei was detected for the reaction between t-butylmagnesium chloride and carbon tetrachloride in bromotrichloromethane. Savin et al.[84] propose that the outcome of the reaction can be represented by a scheme that assumes single-electron transfer at the first stage:

$$(CH_3)_3CMgCl + CX_4 \rightarrow [(CH_3)_3\dot{C}MgCl^+ + C\dot{X}_4^-] \rightarrow (CH_3)_3\dot{C} + \dot{C}X_3 + MgClX.$$

The resulting radical pair disproportionates in two ways:

$$(CH_3)_3\dot{C} + \dot{C}X_3 \begin{cases} \rightarrow HCX_3 + (CH_3)_2C{=}CH_2 \\ \rightarrow (CH_3)_3CX + :CX_2 \end{cases}$$

as indicated by the ^1H polarisation phase in t-butyl chloride. In this case the high yield of products from the further reaction of dihalocarbene indicates that the reaction mainly occurs by the second route.

However, in the opinion of Davies et al.,[86] while the reaction of CCl_4 with EtMgBr occurs by a radical route (as is indicated by the formation of ethane and ethylene), the reaction of phenylmagnesium bromide, although giving 1,1-dihalonorcarane in the presence of cyclohexene, follows a heterolytic route via trichloromethylmagnesium bromide, which acts as a carbenoid. Thus, there is no common view about the mechanism of the

reactions of organic compounds of the most active metals of Groups I and II with halomethanes, but there is evidence to support radical processes which occur through the acceptance of electrons by tetrahalomethane.

A considerable number of reports on these types of reactions of carbon tetrahalides with OMCs relate to organomercury compounds. It is observed that in contrast to organolithium and organomagnesium compounds they generally react at higher temperatures. Thus, Ph_2Hg starts to react with CCl_4 at 200 °C, as a result of which phenylmercuric chloride, benzene, benzotrichloride, and hexachloroethane are formed.[87]

It is assumed that the initial stage of the reaction of organomercury compounds with CX_4 is dissociation of the OMC to radicals.[88–90] The free-radical pathway for the process has been confirmed by the inhibitor method.

Photolysis of organomercury compounds, which gives free radicals, assists the reaction, and in this situation it occurs even at room temperature.

Organic peroxides also have an initiating effect on the reaction between organomercury compounds and tetrahalomethanes.[91] A mechanism that includes a single-electron transfer stage has been proposed for reactions involving peroxides:[92]

$$\begin{matrix} R{-}Hg{-}OR \\ + \\ Cl{-}CCl_3 \end{matrix} \rightarrow \left[\begin{matrix} R{-}Hg^{+}\ \dot{O}R \\ Cl^{-}\ \dot{C}Cl_3 \end{matrix} \right] \rightarrow RHgCl + RO^{\cdot} + {}^{\cdot}CCl_3.$$

It is thought in this case that the catalytic effect of the peroxide consists essentially of forming a complex with the OMC, in which an additional polarisation of the carbon–metal bond occurs and hence the reactivity of the OMC towards the tetrahalomethane is increased. Strongly solvating media (dioxan, pyridine, hexamethylphosphotriamide) appear to have a similar effect.[93]

Tetrahalomethanes, in particular CCl_4, exhibit their electrophilic properties not only in the case of reactions with OMCs but also with other carbanion sources. These can be strong CH-acids which generate a carbanion *in situ* on treatment with different bases. The main course of the reactions, as in the case of OMCs, is halogenation of the carbanion. However, dimerisation can quite often be an alternative reaction.

Thus, by treatment with CCl_4 and lithium diisopropylamide or with alkali in alcohols it is possible to halogenate diarylmethanes,[94] ketones,[95,96] sulphones,[97,98] and saturated and unsaturated ethers.[99] Apart from CCl_4, CBr_4 or CCl_3Br can also act as halogenating agents.[99] It is interesting to note that in the latter case α-bromination of the carbanion mainly occurs, which is an indication of the greater ease of transfer of the bromine atom.

Phase-transfer catalysis is particularly promising for the halogenation of CH-acids with tetrahalomethanes. In the system concentrated alkali–triethylbenzylammonium chloride, halogenation of phenylacetylene,[100] 2-phenylalkyl nitriles,[101] and arylbenzyl ketones,[102] readily occurs. Dimerisation is possible as a side-reaction:[103]

$$PhCH_2CN + CCl_4 \rightarrow PhC(CN)=C(CN)Ph,$$
$$Ph_2CHCN + CCl_4 \rightarrow Ph_2C(CN)-C(CN)Ph_2.$$

It is assumed that halogenation of the carbanion occurs through the formation of a radical–radical anion pair as a result of discrete electron transfer,[96,99] for example:

$$\ominus\!\cdot\!\cdot\!\cdot\!\overset{O}{\overset{\|}{C}}H_2{-}C{-}OR \xrightarrow{CBr_4} \left[\ominus\!\cdot\!\cdot\!\cdot\!\overset{O}{\overset{\|}{C}}H_2{-}C{-}OR\ \ \dot{C}Br_4^{-} \right] \rightarrow \overset{O}{\overset{\|}{Br}}CH_2{-}C{-}OR + \ominus CBr_3.$$

It should be noted that a similar approach to the reactions of carbanions with alkyl halides has generally been actively discussed recently.[104]

V. Reactions with electron-neutral nucleophiles

The electrophilic properties of carbon tetrahalides are exhibited in the formation of complexes with different *n*- and π-donors. However, in this case also the coordination site is not carbon but a peripheral halogen atom. It is to be expected that this route is taken in the self-association of CX_4 molecules (X = Cl, Br, I),[105] which disappears on addition of cyclohexane,[106] if it is assumed that such an association occurs through the interaction of the UEP of the halogen atom (as an *n*-donor) with the antibonding orbital of the C–X bond of neighbouring molecules as occurs in intermolecular X...X contacts in these compounds in the crystalline state.[38,39]

Interactions of a similar type apparently occur on mixing carbon tetrachloride with ethers, which act in this case as *n*-donors.[107]

It is well known that the π-electron properties of aromatic hydrocarbons have an effect on their ability to form complexes with various electron acceptors, including tetrahalomethanes. Thus, it has been known for quite some time that carbon tetrachloride and tetrabromide form crystalline complexes with benzene,[108,109] toluene,[109] and polymethylated benzenes.[110] X-Ray diffraction analysis of the complex between CBr_4 and *p*-xylene showed that in a crystal molecule of the partners alternate in small chains, in which each halide molecule is bonded to two molecules of aromatic compound via bromine atoms. In this case the distance between the bromine atom and the centre of the plane of the hydrocarbon ring is less than the sum of the van der Waals radii.[112] When the halogen nuclei were studied by NQR it was not possible to come to any conclusion about the nature of the bonding in these complexes,[113] but the data of IR spectroscopy suggest that in hydrocarbon–tetrahalomethane mixtures, complexes of composition 1:1 are apparently formed by charge transfer.[114,115] The changes in the Raman spectra of a solution of CCl_4 in benzene and mesitylene are interpreted as resulting from charge transfer from the π-donor to the chlorine atom.[116] It is thought in this case that an electron can be accepted either via the σ* orbital of the carbon–halogen bond[113] or via vacant 3*d* orbitals of the halogen atom.[116,117]

Reactions of tetrahalomethanes with neutral nucleophiles such as tricoordinate nitrogen or phosphorus compounds occupy a special place in terms of the quantity of information as well as the chemical effects. It is therefore worth examining them in greater detail.

The instability of solutions of amines in carbon tetrachloride was observed some time ago.[118–120] On standing in glass vessels, a precipitate is rapidly deposited from this mixture and chloroform is formed. It is thought that the cause of this instability is the formation of a charge-transfer complex between the reactants. The existence of such complexes has been confirmed by UV spectroscopy for the systems $NH_3{\cdot}CCl_4$, $NH_3{\cdot}CBr_4$,[121] $Et_3N{\cdot}CCl_4$, $Et_3N{\cdot}CBr_3Cl$,[120] and $Bu_3N{\cdot}CCl_4$.[122] Recently crystalline complexes of carbon tetrabromide with diazabicyclo[2.2.2]octane (DABCO) and quinuclidine were successfully isolated and studied using X-ray diffraction analysis.[123] It was shown that the molecular structure of the complex between CBr_4 and DABCO is in the form of sinuoidal chains in which the diamine is coordinated with the halogen atoms of two tetrahalide molecules, while quinuclidine forms discrete donor–acceptor pairs.

Since the formation of complexes in these cases, in the opinion of the authors, assumes that there is an interaction between the UEP of the donor and the σ^* orbital of the C–X bond, this transition to some extent neutralises the bonding due to the two electrons situated in the σ orbital. Therefore, on irradiation in the near-UV region dissociation of the complex can occur,[124] resulting in the formation of radical-ion pairs

$$\left[\equiv N\cdot CBr_4\right] \xrightarrow{h\nu} \left[\equiv \dot{N}^{+}\, \dot{C}Br_4^{-}\right],$$

whose reactions account for the photochemical instability of the solutions of amines and tetrahalomethanes. Thus, on irradiation of $RNH_2\cdot CCl_4$ with visible light at $\lambda = 2537$ Å in the absence of oxygen, $R\dot{N}H_3\ Cl^-$, $CHCl_3$, C_2Cl_6, $R'CH=NR$, and NH_3 are formed, with a quantum yield ranging from 1 to 100.[122] The formation of these compounds results from the following series of reactions:

$$RNH_2\cdot CCl_4 \xrightarrow{h\nu} R\dot{N}H_2\ Cl^- + \dot{C}Cl_3,$$
$$R\dot{N}H_2\ Cl^- + RNH_2 \rightarrow R\dot{N}H_3\ \dot{C}l^- + R\dot{N}H,$$
$$\dot{C}Cl_3 + RNH_2 \rightarrow CHCl_3 + R\dot{N}H\ (\text{or}\quad R'\dot{C}HNH_2),$$
$$R\dot{N}H\ (R'\dot{C}HNH_2) + RNH_2 \rightarrow R'CH=NH + R\dot{N}H_3\ Cl^-,$$
$$R'CH=NH + RNH_2 \rightarrow R'CH=NR + NH_3,$$
$$2\dot{C}Cl_3 \rightarrow C_2Cl_6.$$

When the reaction is carried out in the presence of oxygen, the molar ratio of the reaction products varies and, moreover, *N,N'*-dialkylureas are formed, apparently by the reaction of the amine with phosgene that occurs as a result of the radical oxidation of CCl_4.

Recently the radical nature of the photochemical reaction of amines with carbon tetrachloride has been confirmed by the occurrence of the effect of chemically induced polarisation of the ^1H nuclei.[125]

The reaction with tetrahalomethanes in the dark and in the absence of oxygen can be initiated with Cu(I), Cu(II), Fe(II), and Fe(III) salts.[126] It is thought that in this case the reaction is radical in nature. In addition, the reaction mixture stimulates the addition of CCl_4 to olefins.[127]

The reactions of tetrahalomethanes, in particular CCl_4, with tricoordinate phosphorous derivatives have become quite widespread in recent times. The greatest attention of research workers has been given to the system Ph_3P-CCl_4, which is a mild selective reagent. This system has been applied most widely in the halogenation of alcohols with a very variable structure and also in reactions that accompany the dehydration and formation of the P–N bond.[128–130]

From the ideas about the electronic structure of tetrahalomethanes and their reactions with both charged and neutral nucleophiles, it is to be expected that the initial stage of the reaction involving the Ph_3P-CCl_4 system should be electron transfer from the phosphorus atom to the σ^* orbital of the C–Cl bond. But while in the case of the amine–tetrahalomethane system homolytic decomposition follows the transfer of electrons, in the case of tertiary phosphines there is heterolysis of the intermediate complex.[129] Nevertheless, it should be noted that on exposure of solutions of Ph_3P in carbon tetrachloride to light, photochemically induced homolytic reactions occur concurrently, as chemically induced polarisation of the ^{31}P nucleus occurs.[131]

Thus, a scheme involving nucleophilic attack by the phosphorus atom on a halogen atom in the tetrahalomethane has been proposed by many authors for reactions that take place in the absence of light and radical initiators:

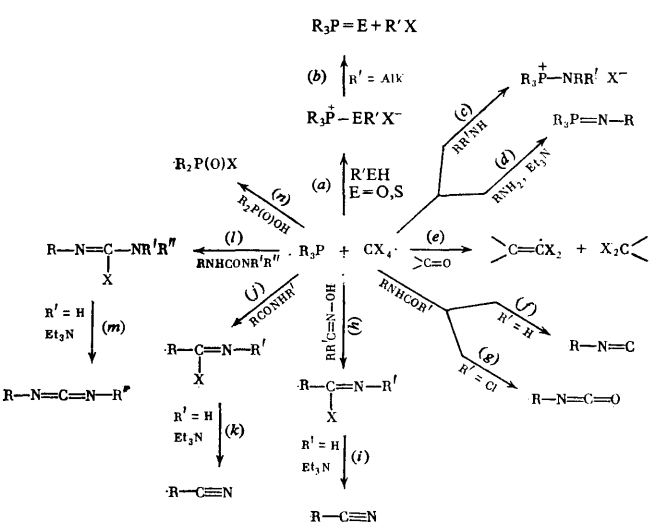
$$R_2(R'_2CH)\,P^{+\delta}\ldots X\ldots \overset{-\delta}{C}X_3 \rightarrow [R_2(R'_2CH)\,P{-}X]^+\ CX_3^- \rightarrow$$
$$\xrightarrow{(1)} R_2(R'_2CH)\,\overset{+}{P}{-}CX_3\ X^-$$
$$\xrightarrow{(2)} R_2P{=}CR'_2 + HCX_3$$
$$\qquad\qquad |$$
$$\qquad\qquad X$$

The resulting dipolar associate is converted to an ion pair with a trihalomethide anion, which, depending on the structure of the phosphorus-containing residue, is converted either to the corresponding phosphonium salt[132] or (when there is an active hydrogen on the α-carbon atom) to haloform and a *P*-halogen ylide by deprotonation.[130] The latter is stimulated on the one hand by an increased CH-acidity and on the other hand by steric shielding of the phosphorus atom. It is observed here that the reactivity of the tetrahalomethane increases on going from CCl_4 to CBr_4 and then CI_4.

Reactions of CX_4 with tertiary phosphines that take place by route (*1*) are not complete when the trihalomethyltriorganylphosphonium halide is formed. In the presence of excess phosphine these very active compounds react further:

$$R_3\overset{+}{P}CX_3\ X^- + R_3P \longrightarrow R_3P{=}CX_2 + R_3PX_2 \longrightarrow \left[R_3P{-}CX_2{-}PR_3\right]^{++} 2X^- \xrightarrow{R_3P}$$
$$\longrightarrow \left[R_3P{=}C(X){-}PR_3\right]^{+}\ X^- + R_3PX_2\,.$$

It is assumed that the formation of triorganylhalophosphonium trihalomethide $R_3P^+Hal\ CHal_3^-$ at an intermediate stage of the reaction permits a considerable number of reactions involving tertiary phosphines and tetrahalomethanes to take place.[129]



The system tertiary phosphine–tetrahalomethane–hydrogen donor has been used successfully to obtain quasiphosphonium salts from phenols or thiophenols (*a*) and also alkyl halides from alcohols (*b*). By introducing secondary amines into the reaction it is

possible to obtain aminophosphonium salts (*c*). Phosphinic acids can readily be converted to their acid halides (*n*). For the purposes of organic synthesis an R_3P-CCl_4 mixture can be used for the preparation of chloroformamidines from trisubstituted ureas (*l*) or imidoyl halides from *N*-substituted carboxamides (*j*) and ketoximes (*h*). When carbamoyl halides are used it is possible to obtain isocyanates (*g*).

If the compound that acts as a hydrogen donor contains two active hydrogen atoms, conducting the reaction in the presence of triethylamine as a halogen halide acceptor has the result that dehydrohalogenation takes place by a route different from route (*c*) [reactions (*d*), (*f*), (*i*), (*k*), and (*m*)].

The use of the binary system R_3P-CX_4 to obtain 1,1-dihaloalkenes from aldehydes and ketones has been reported. Dihaloalkenes are probably obtained from an intermediate triorganylhalomethylenephosphorane as the result of a Wittig reaction (*e*).

The use of the system R_3P-CX_4 for halogenation of the hydroxyl group has been described in great detail.[128,129] However, during the time that has passed since these reviews were written, a large quantity of additional information has been published.

A considerable number of studies have been devoted to establishing the mechanism of this reaction. It has been shown conclusively that the reaction takes place via an intermediate alkoxyphosphonium salt, which then undergoes an S_N2 substitution.[133,134]

$$Ph_3P + CCl_4 \rightarrow Ph_3\overset{+}{P}-Cl\ CCl_3^- \xrightarrow{ROH} Ph_3\overset{+}{P}-OR\ Cl^- + HCCl_3,$$
$$Ph_3\overset{+}{P}-OR\ Cl^- \rightarrow Ph_3P{=}O + RCl.$$

Sometimes this salt can be separated as a stable hexafluorophosphorate.[135]

In recent times interest has mainly been directed towards using this sytem Ph_3P-CCl_4 for the halogenation of polyols.[136-140] It is observed that the reaction is selective, namely, only a primary hydroxyl group undergoes transformation. However, intramolecular cyclodehydration to an α-oxide can occur as a subsequent stage.[138,139]

There is continued interest in the use of systems containing CX_4 and diphenylphosphinated polymers for the halogenation of alcohols, giving higher yields of products than the binary system Ph_3P-CX_4.[141,142]

The system Ph_3P-CCl_4 has been used to obtain cyclic and acyclic 1,2-dichloroalkanes from α-oxides[143] and for the synthesis of 1,1-dichloroalkenes from the corresponding carbonyl compounds.[144,145]

In addition to the widely used carbon tetrachloride, other symmetric tetrahalomethanes have started to be used for halogenation of the OH group. It is observed in this case that CBr_4 and CI_4 react more readily than their chlorine analogue,[140,146-148] while in the case of CF_2Cl_2 only a chlorine atom participates in the reaction.[149]

The system CBr_4-PPh_3 has been quite widely used for the selective halogenation of primary hydroxyl groups in sugars and nucleosides.[140,146-147] It can be used to dehydrate amides, aldoximes, and ureas to the corresponding nitriles and carbodiimides after a shorter period of time and at a lower temperature than in the case of Ph_3P-CCl_4,[150] and there is a much greater ease in forming the ylide $Ph_3P{=}CBr_2$, which then either undergoes alkylation by alkyl halides to the corresponding phosphonium salts[151] or gives dibromoolefins by the Wittig reaction.[152,153] The quantitative polycondensation of *p*-aminobenzoic acid is achieved using the system CBr_4-PPh_3.[154]

The bromine atom in $BrCCl_3$ is attacked very readily by tertiary phosphines. This is suggested by the formation of only $Ph_3P{=}CCl_2$ [155,156] and also the preparation of bromophosphazo compounds from phosphinous acid anilides.[157]

The fluorine atom in fluorine-containing tetrahalomethanes CF_nX_{4-n} (X = Cl, Br, I; $n = 1-3$) is never attacked by tertiary phosphines. In all cases transfer of the more polarisable halogen occurs. This is suggested by the formation of $Ph_3P{=}CFX$ in the reaction of Ph_3P with CFX_nY_{3-n}, where X and Y = Cl, Br, I,[158] and by the trifluoromethylation of silicon chlorides R_nSiCl_{4-n} with the binary system $(Et_2N)_3P-CF_3Br$.[159]

$$(Et_2N)_3P + CF_3Br \rightarrow (Et_2N)_3\overset{+}{P}-Br\ CF_3^- \xrightarrow[-(Et_2N)_3PBrCl]{Me_3SiCl} Me_3SiCF_3.$$

It is thus possible to replace one or two chlorine atoms on silicon in organylchlorosilanes with the trifluoromethyl group. Similarly trifluoromethyl P(III) derivatives are formed if a tricoordinate phosphorus halide is introduced into the reaction as the third component.[160]

The stability of the C–F bond in tetrahalomethanes is confirmed by the formation of 1,1-difluoroolefins in the reaction of carbonyl compounds with a mixture of $(Me_2N)_3P-CF_2Br_2$ [161] or 1,1-difluorocyclopropanes as a result of the reaction of this system with disubstituted alkenes.[162]

1,1-Diiodoalkenes are formed in good yield when the binary system CI_4-Ph_3P is treated with aldehydes.[163]

The reaction of white phosphorus P_4 with CCl_4 may also be regarded as a process that involves reactions between tricoordinate phosphorus derivatives and tetrahalomethanes. Treatment of this reaction mixture with alcohols or phenols leads to the formation of phosphite esters[164,165] and treatment with thiols gives their thio analogues.[166]

Reactions of esters of tricoordinate phosphorus acids with tetrahalomethanes also play an important role in synthetic organophosphorus chemistry:

$$\rangle P-OR + CX_4 \rightarrow \rangle P\begin{matrix}O\\ \diagdown CX_3\end{matrix} + RX.$$

Those reactions with carbon tetrachloride are the most common. It reacts with phosphite,[128,167,168] phosphonite,[130,169,170] and phosphinite[171-174] esters and also with phosphorus acid ether amides.[175,176]

As a rule P(III) acid esters react with CBr_4 more readily than with CCl_4.[128,130] Among the other tetrahalomethanes that take part in reactions with phosphinites, mention should be made of $CBrCl_3$,[177,178] $CFBr_3$, and CF_2Br_2.[179]

As far as the mechanism of these reactions is concerned, at the present time the idea is becoming established that in the absence of radical initiators, in the dark, and when there is steric hindrance at the phosphorus atom, a heterolytic reaction takes place by means of attack by the phosphorus-containing nucleophile on a halogen atom:

$$\rangle P-OR + X-CX_3 \rightarrow RO-\overset{+}{P}\begin{matrix}\diagup X\ CX_3^-\\ \diagdown\end{matrix} \rightarrow$$
$$\rightarrow RO-\overset{+}{P}\begin{matrix}\diagup CX_3\ X^-\\ \diagdown\end{matrix} \rightarrow \rangle P\begin{matrix}-CX_3\\ \| O\end{matrix} + R-X.$$

This relates to the reactions of $(RO)_3P$,[180] $RP(OR)_2$,[130,169] $(Me_2N)_2POR$,[176] R_2POR,[171,173] and $(R_2N)_2PSR$.[181]

It has been observed that the reactivity of P(III) acid esters towards CCl_4 varies in accordance with the following series:[176,182]

$$iso\text{-}PrO)_3P > (EtO)_3P > (MeO)_3P > (EtO)_2POPh > EtOP(OPh)_2 \gg P(OPh)_3.$$

This sequence matches the increase in the half-wave potential of the anodic oxidation of P(III) acid esters,[183] which is proportional to the HOMO energy. Thus, it may be assumed that these processes between CX_4 and tricoordinate phosphorus acid esters correspond to a donor-acceptor interaction between P(III) compounds and tetrahalomethanes and in this respect there is a perfect similarity between them and the reactions of tertiary phospines depicted above.

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The analysis carried out on the structural features and reactivity of carbon tetrahalides indicates that, in contrast to the widely known chemical inertness of CF_4, its analogues exhibit a large number of reactions on treatment with electron donors. These properties of CX_4 molecules, where X = Cl, Br, and I, are apparently due to the energy accessibility of σ-type antibonding molecular orbitals of the C–X bonds, which accounts for the coordination of the reactants on a peripheral halogen atom rather than on the carbon atom, resulting eventually in halogen transfer.

It cannot be excluded that similar reactions occur in the case of tetrahalides of other elements.

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High speed autowave reaction regimes in low-temperature solid state chemistry

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ABSTRACT. The results of studies on new phenomena of the travelling wave type in low-temperature solid state chemistry, observed in a wide variety of solid-state chemical reactions at the temperatures of liquid nitrogen or helium, are surveyed. The processes investigated are characterised by anomalously high rates of reaction for the temperature range indicated, comparable to the rates of the fastest high-temperature combustion reactions in classical chemistry. A mechanism is proposed with an autocatalytic mechanochemical step which permits a qualitative explanation of all the characteristic features observed in the phenomenon. It is suggested that the mechanism indicated occurs widely in space chemistry and in the processes involved in the chemical evolution of the universe.

The bibliography includes 67 references.

Contents

I.	Introduction	205
II.	Objects of study	206
III.	Activating role of brittle breakdown in the reaction excitation stage	206
IV.	Autowave reaction regimes	207
V.	Theory of autowave processes in solid-phase cryochemical reactions	208
VI.	Autowave reactions under the conditions of uniform compression and the role of mechanical stress dynamics	210
VII.	Expansion of the range of systems investigated (new types of autowave process)	211
VIII.	Conclusion	214

I. Introduction

Quite recently, at the beginning of the 1970s, the very possibility of a chemical reaction in the solid state near the absolute zero of temperature appeared doubtful (electron transfer reactions[1] in the solid state at low temperatures are not considered in this review). An event which made it necessary to revise the existing ideas was the discovery of the phenomenon of the low-temperature limit of the rate of a chemical reaction in relation to the radiation-initiated polymerisation of formaldehyde;[2] the existence of this phenomenon was subsequently established in a number of other chain and non-chain reactions (see Gol'danskii et al.[3] and the references therein). It was discovered that there exist systems in which a reaction occurs even at the temperature of liquid helium at a low but entirely measurable rate, which is independent of temperature. In order to account for the phenomenon of the low-temperature limit in cryochemical reactions, the concept of molecular tunnelling was put forward. It was subsequently developed taking into account low-temperature intermolecular interactions (see Gol'danskii and co-workers[3–7] and the references therein).

A fundamentally new factor in the introduction of the concept of the tunnel mechanism into the kinetics of low-temperature radiation-initiated chain reactions in the solid state was the assumption of the energy equilibrium in the reacting solid-phase system. However, the universality of the proposed kinetic models for the processes indicated, wholly based on the classical ideas of equilibrium Arrhenius kinetics, was never regarded as axiomatic, particularly since the subject under consideration consisted of various chemical reactions stimulated by ionising radiation supplied from the outside, i.e. under conditions where temperature ceases to be the only parameter characterising the energy state of the system.

The appearance of alternative mechanisms, according to which the leading role in low-temperature solid-phase reactions was attributed to non-equilibrium states, was entirely natural. As early as 1960, Semenov[8] proposed a mechanism involving energy chains in order to describe the radiation-stimulated solid-phase polymerisation. According to this mechanism, the energy evolved in each elementary step during the growth of the polymer chain ensures the overcoming of the activation barrier in the next step of this kind. The polymer chain can grow via this mechanism at the rate of propagation of the exciton ($\sim 10^6$ mm s^{-1}). This exciton chain model has been examined theoretically in detail.[9] The important conclusion was reached that very high rates of a solid-phase reaction really occur even at very low temperatures as a result of the chain transfer of energy via the frozen matrix.

A combined mechanism, assuming the operation of the tunnel mechanism in the reaction initiation stage, postulating the subsequent very rapid development of a chain process as a result of the recovery of the energy of the reaction steps, has been described.[10]

Together with this chain-tunnel mechanism, mention should be made of yet another combined mechanism. This is the chain-thermal mechanism proposed and developed[11–13] in order to interpret the limiting phenomena in the accumulation of radicals during the irradiation of frozen specimens of different organic substances.

Here however we should like to draw attention not to the difference between the equilibrium tunnel mechanism and the mechanisms of the non-equilibrium type but to the simplifying assumption, from which all these approaches have originated, and which must be abandoned in many instances. This topic will be dealt with later in the review.

The point is that in the models investigated the solid matrix itself was regarded in essence from a single standpoint, namely as a kind of ideal defect-free system in mechanical equilibrium. In other

words, in the analysis of the phenomena the fact that the systems investigated are characterised by a significant mechanoenergetic disequilibrium was rejected. This quality of the specimens actually studied was a consequence of both the conditions in their preparation and of the effect of fluxed of ionising radiation. It is known that the initial spatial disposition of the molecules is significantly distorted in the irradiated solid, the phase state of the solid is modified, homogeneity is affected, the internal stresses field is greatly altered, and the strength characteristics are appreciably reduced. The transition in the experiments to the post-effect conditions does not eliminate the problem of the role of the mechanical disequilibrium of the specimen in the solid-phase reaction because the specimen remains a significantly non-equilibrium object even after the γ-ray energy flux has been switched off because of the retardation at low temperatures of all kinds of relaxation processes. Apart from the factors quoted, the chemical reaction itself, which has been initiated in the solid matrix, must be a source of intensification of distortions in the lattice i.e. of further accumulation in the latter of mechanical potential energy

The considerations described above served as a starting point in the formulation of tasks in a series of studies[14–24] The factor which stimulated the consideration of the mechanochemical aspect of the radiation cryochemistry of the solid state was the observation[14] of initiation of the reaction by a local break in irradiated specimens stabilised by a low temperature.

The principal questions can be briefly formulated in the following way. Can one liberate the potential energy accumulated in the mechanically non-equilibrium matrix of the frozen specimen of the reactants by its brittle breakdown. Will the stored mechanical energy be transformed into chemical energy and will a chemical reaction occur under these conditions?

The possibility of a positive answer to these questions was supported by the general postulates of the theory of the strength of a solid, from which it followed that the mechanical energy of the elastic deformation at the instant when the break occurs is concentrated in the region directly adjoining the surface being formed. It is known[25] that this energy transformation process is accompanied by a significant change in the physicochemical properties of the substances on the freshly formed surface compared with the bulk-phase properties: the brittle breakdown is coupled with phenomena such as electron and ion emission, luminescence, the formation of radicals, and a sharp acceleration of transport processes on the cleavage planes. In other words, it appeared likely that the transition of the process from the homogeneous regime to a significantly heterogeneous regime via the brittle breakdown of the specimen involves a non-equilibrium mechanism of energy transfer to active centres previously "frozen" in the three-dimensional matrix and induces thereby a chemical reaction at low temperatures. To the foregoing, one should add that in the traditional mechanochemical processes, a notable role was always attributed to brittle breakdown (although it did occur under the conditions of forced dispersion of the specimen) (see Lyakhov and Boldyrev[26] and the references therein).

We may note yet another factor which has stimulated a revision of the existing ideas. In previous studies, both the kinetic models themselves, describing the solid-phase radiation-chemical reactions, and the experimental methods were based on the assumption that the system is uniform and that the chemical reaction is homogeneous. This stage was entirely natural because, with the aid of calorimetric and spectroscopic methods using an integrated signal, it was difficult to discover and investigate the characteristic features of non-uniform chemical reaction regimes. We may note that doubts about the admissibility of the application of zero-dimensional kinetic models in the radiation chemistry of the solid state have always existed, because it is well known that an irradiated specimen is never homogeneous (highly active regions, tracks and spurs, arise during radiolysis and the stabilising radicals and ions are distributed non-uniformly throughout the space within the body). Apart from the neglect of the inhomogeneity factor in the development of the process throughout the specimen, the homogeneous approach was also restricted by the fact that it did not make it possible to go outside the framework or linear (or almost linear) kinetic models and hindered the discovery of the features of significantly non-linear mechanisms—mechanisms with feedback. Nevertheless, their existence in complex chemical systems such as a reactive solid had to be regarded as extremely likely. In particular, the existence of feedback between the mechanical state of the system and its chemical activity is extremely probable. These considerations also stimulated the study of the role in the solid-phase processes investigated of all kinds of artificially introduced or spontaneously arising local perturbations.

The selected approach justified itself, the initial postulates proved to be legitimate, and the investigations led to the discovery of highly intense autowave regimes in low-temperature solid-phase reactions. The principal results of this first stage of these studies have been surveyed in a previous review.[27] In order to maintain a logical consistency, certain fundamental conclusions arising from previous studies were introduced into the present review, which is devoted to the analysis of the state of the problem of autowaves in cryochemistry of the solid state at a new stage of its investigation.

II. Objects of study

The objects of study[27] were systems in which a spontaneous development of reaction chains is impossible in the solid state at radiolysis temperatures of 77 and 4.2 K. In the course of the γ-irradiation of these solid-phase systems at the nitrogen and helium temperatures, non-chain radiation-chemical reactions take place and lead to the formation of energy-rich active centres which are chemically stable in the temperature range indicated. Various classes of reactions have been investigated: chlorination of hydrocarbons, chlorination and hydrobromination of alkenes, polymerisation, etc. The characteristic features of solid-phase reactions were investigated in the first stage in the following systems: (1) a vitreous solution of chlorine in butyl chloride (molar ratio 1:3, glass point $T_g \simeq 100$ K);[28] (2) a vitreous solution of chlorine in methylcyclohexane (ratio 1:3, $T_g \simeq 93$ K);[14] (3) the crystalline complex $C_2H_4.HBr$ (T_m† = 110 K);[29,30] (4) a vitreous solution of SO_2 in 2-methylbuta-1,3-diene (ratio 1:1, $T_g \simeq 110$ K).[17]

III. Activating role of brittle breakdown in the reaction excitation stage

In order to achieve the brittle breakdown of the specimen, the method involving the induction of thermoelastic stresses by selecting a rate of change of the specimen temperature sufficient to induce cracking was applied initially. The rate of change of temperature was recorded and the thermal signals accompanying the breakdown

† Melting point (Ed. of translation).

were observed with the aid of a differential scanning calorimeter (for a more detailed description of the method, see Barkalov et al.[31]).

When the specimens are heated slowly from 4.2 to 77 K, which does not lead to cracking, the calorimeter does not reveal any thermal effects (Figs. 1*a* and 1*b*, continuous lines). Rapid heating induces the cracking of the specimen and the accompanying thermal effect is recorded by the calorimeter (Figs. 1*c* and 1*d*, continuous lines). After selecting a rate of change of temperature such that the specimen cracks, similar experiments were carried out but this time with specimens treated with a definite dose of ^{60}Co radiation (in order to create stabilised active centres in the system). During slow heating of the irradiated specimen, unaccompanied by its cracking, the system remained chemically inert, i.e. thermal effects were not recorded (Figs. 1*a* and 1*b*, dashed lines). At a high heating rate, a chemical reaction was initiated at the instant of the brittle breakdown of the specimen (Figs. 1*c* and 1*d*, dashed lines).

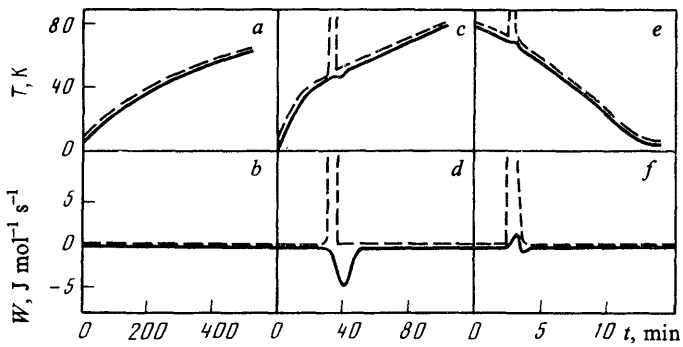


Figure 1. Time variation of the temperature of a vitreous solution of chlorine in methylcyclohexane (*a*, *c*, *d*) and of the accompanying thermal effects (*b*, *d*, *f*): continuous—non-irradiated specimen; dashed lines—specimens irradiated with ^{60}Co γ-rays at 77 K at a dose of 27 kGy.

The brittle breakdown of the specimen and the accompanying chemical reaction were achieved also on rapid cooling. Figs. 1*e* and 1*f* present data obtained on fairly rapid cooling of the specimen inducing the cracking of the solid matrix. Evidently the cracking of the irradiated specimen was accompanied by a chemical reaction (there was no reaction in the non-irradiated specimen).

In order to demonstrate the decisive role of the formation of cracks as a factor initiating the chemical reaction, a direct experiment was formulated involving a non-thermal disruption of the solid mixture of reactants. The cracking was achieved at a constant thermostat temperature of 4.2 K by rotating a thin metallic rod frozen into the specimen. At the instant of the introduction of such perturbation into the matrix containing the stabilised active centres, a rapid, one might say "explosive", chemical reaction occurred. Despite the local initiating, the reaction spread throughout the cell—the dark colour induced by the γ-radiolysis vanished.

The results described above permitted two fundamentally important conclusions: (1) in the systems investigated, brittle breakdown induces an abrupt solid-phase chemical reaction and (2) the development of the process initiated by the cracking of the specimen is self-accelerating and involves the entire specimen. Consequently the formation of the primary crack plays the role of an initiating device incorporating a positive feedback mechanism, which ensures a self-maintaining process regime. In order to elucidate this mechanism, experiments were formulated in order to investigate the dynamics of the reactions developing in this system in response to the perturbation introduced.

The observed features of the dynamics of the development of an abrupt reaction demonstrated convincingly that the classical thermal feedback mechanism is not decisive in the given instance. The establishment of the leading role of the surface formed on disruption of the matrix made it possible to formulate the following hypothetical non-thermal mechanism of the self-activation of the system investigated: the chemical reaction arising on the cleavage planes and in the adjoining regions generates in its turn breaks in continuity in the regions of the solid matrix not involved in the reaction (for example, as a consequence of the appearance during the reaction of temperature or density gradients, which create stresses disrupting the specimen). This model, which can be classified as of the branched-chain type, describes qualitatively a number of experimentally observed facts, namely: (1) the critical phenomena involving the appearance and spontaneous self-accelerating development of a reaction accompanied by intense dispersion of the solid matrix comprising the reactants; (2) the initiation of a similar explosive process by creating in the initial instant an initiating network of cracks by the mechanical or thermal disruption of the specimen (in the absence of such perturbations, the rate of reaction is immeasurably small); (3) the degeneracy of critical phenomena (see the bibliography in the paper of Barelko et al.[27]).

IV. Autowave reaction regimes

It is known that a fundamental feature of the systems described by non-linear branched-chain models is autowave phenomena characteristic of such systems. The autowave reaction regimes should arise in sufficiently large specimens in response to a locally introduced perturbation.

On the other hand, in the first experiments[16] it proved possible to initiate the spontaneous propagation of the reaction wave by means of a local perturbation (by creating a local cleavage plane in the specimen as a result of mechanical action or by supplying a thermal pulse disrupting a limited region in the solid matrix). The characteristic results obtained in experiments with a cylindrical specimen of a frozen mixture of reactants 0.5–1.0 cm in diameter and 5–20 cm long are presented below. Since the reaction was accompanied by a change in the colour of the specimen, the velocity of the fronts was measured successfully using the possibilities of cine-techniques. The cinegrams show clearly how the front, propagated parallel to itself along the axis of the cell at a constant rate of 1–2 cm s^{-2}, is formed on local mechanical breakdown.

In order to investigate the structure of the wave front (its temperature profile), a series of thermographic experiments on the autowave process were carried out. The rate was determined from the time taken by the waves to traverse the distance between two thermocouples frozen into the specimen.[16–18]

Fig. 2 presents the characteristic profiles of the travelling temperature waves (in terms of time and spatial scans) for initial temperatures of 77 K (*a*) and 4.2 K (*b*). The form of the profile does not undergo qualitative changes when the thermostat

temperature is altered. The process consists of the following stages: *AB*—inert heating (at 77 K, this stage was not recorded, i.e. was almost isothermal); *BC*—abrupt start and explosive course of reaction (characteristic break at point *B*); *CD*—cooling stage. The *BC* stage is rapid. The oscillograph scan of this zone of the running wave front shows that at 77 K (Fig. 2*a*) the duration of the given stage is ~0.1 s, i.e. at a wave velocity $U \simeq 20$ mm s^{-1} the zone width is $\delta \simeq 0.2$ cm, while at 4.2 K (Fig. 2*b*) the duration of the stage is ~0.3 s and the width is $\delta \simeq 0.3$ cm (wave velocity $U \simeq 10$ mm s^{-1}).

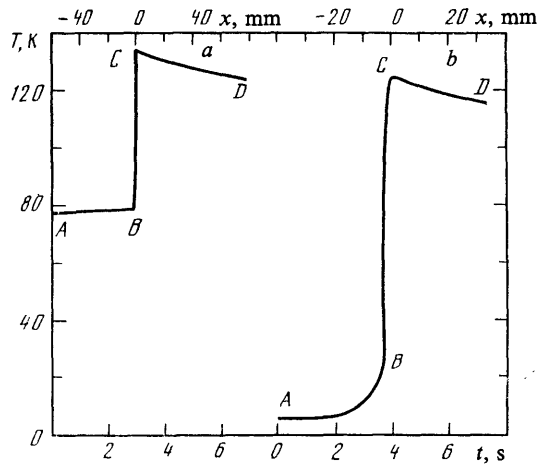


Figure 2. Time and spatial scans of the characteristic temperature profiles of the $C_4H_9Cl + Cl_2$ reaction propagation waves at 77 K (*a*) and 4.2 K (*b*): *a*, $U = 20$ mm s^{-1}; *b*, $U = 10$ mm s^{-1}. Preliminary irradiation dose 27 kGy.

In the structure of the travelling front of a low-temperature reaction presented, it is possible to see clearly features which are completely atypical for classical thermal self-propagation processes: (1) the stage of the inert pre-explosion heating is weakly expressed or is altogether absent; (2) the reaction starts and stops abruptly (characteristic breaks at points *B* and *C*), the reaction at point *B* starting at temperatures significantly lower than the temperature of the onset of the thermally activated reaction ($T_g \simeq 100$ K); (3) the dynamic picture of the development of the process in the spontaneous layer-by-layer initiation of the reaction by the travelling wave is identical with the picture of the forced initiation of the reaction by impact heating; (4) the rate of propagation of the wave changes only slightly on reducing the temperature from 77 to 4.2 K despite the marked alteration of the heat evolution.

The next important step in the elucidation of the role of the thermal factor in the mechanism of the phenomena investigated involved the study of the influence of the size of the specimen on the characteristics of the autowave process.[20] Can the self-maintaining wave regime of the reaction be precluded by intensifying the heat evolution as a result of the reduction of the diameter of the cylindrical tube with the frozen mixture of reactants?

When the experiments with travelling waves were carried out in capillaries 0.5–1.0 mm in diameter (which corresponds to an increase in the parameter characterising the intensity of heat evolution by more than an order of magnitude), it was established[20–22] that there is no degeneracy of the autowave process under these conditions in any of the systems considered. Furthermore, it was discovered that the characteristic rates of autopropagation of the reaction do not undergo any appreciable changes under these conditions.

In the course of development of the relevant research, a series of experiments were performed with thin film specimens of the reactants.[22,27] The experiments were carried out with films frozen onto a flat support and immersed in liquid nitrogen, i.e. under conditions where there was no shield between the surface of the film and the bath of the cooling agent. When the films were punctured or scratched, an autowave process was excited. The use of such objects made it possible to achieve quasi-isothermal process conditions and to promote thereby the manifestation of the isothermal mechanism mentioned above, consisting of the layer-by-layer self-dispersion of the specimen as a result of the difference between the densities of the initial reactants and the final reaction products. Under these conditions, the autowave was not only not suppressed but actually became even more pronounced.

V. Theory of autowave processes in solid-phase cryochemical reactions

The experimental results made it possible to formulate in greater detail the hypothesis concerning the mechanochemical nature of the self-activation of the solid-phase reaction and to construct a tentative qualitative picture of the development of the autoclave process in a chemical interaction in the systems under consideration. The occurrence of the process can be represented as the movement in the solid specimen of a narrow zone extensively intersected by a dense network of freshly formed cracks. The chemical reaction arises in precisely this zone on the surface of the cracks (or near them) and creates in its turn conditions for the continuation of the breakdown in the neighbouring layer of the solid matrix. Such layer-by-layer dispersion of the specimen is induced by the propagating field of the stress, which can be generated, as already stated, either by the difference between the densities of the initial reactants and of the final products (isothermal mechanism) or by the appearance in the specimen of steep temperature gradients as a result of the exothermicity of the reaction (a non-isothermal mechanism). Naturally, these two factors can also operate simultaneously. The non-isothermal mechanism has been analysed[18] in relation to massive cylindrical specimens in which, as shown above, significant heating can take place due to the reaction and the role of thermal stresses in the dispersion steps should be very notable.

The model considered[18] was constructed on the basis of the following assumptions. It is assumed that the specimen is infinite in size and no account is taken of the heat exchange with the surrounding medium, i.e. it is assumed that the characteristic time for the evolution of the heat of reaction is much shorter than the characteristic time for the removal of heat. These conditions constitute the basis for the analysis within the framework of a one-dimensional model. According to the hypothesis, the initiation of the reaction in the given section of the specimen occurs when a stress exceeding the tensile strength of the solid matrix is generated. Since one is dealing with thermal stresses and the region of elastic deformation and brittle breakdown is considered, it follows that, in relation to the given physical model, the stresses can be replaced by temperature gradients assuming that there is an unambiguous

correspondence between them (Fig. 3). Such change of variables greatly simplifies the model and makes it possible to exclude from consideration mechanical equations and to reduce the analysis to only one heat balance equation in which, instead of the limiting brittle breakdown stress, a critical value of the temperature gradient is introduced as the parameter.

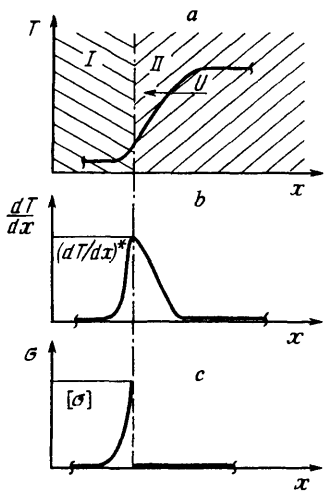


Figure 3. Characteristic form of the temperature profile (*a*), the temperature gradient (*b*) and the stresses field (*c*) in the running wave front: (I) zone of the specimen not involved in the reaction; (II) zone of the specimens dispersed as a result of the reaction.

Taking into account the assumptions made, the equation describing the autowave process assumes at first sight a form analogous to the fundamental equation of the theory of combustion:[32]

$$\lambda \frac{d^2T}{dx^2} - Uc\rho \frac{dT}{dx} + Q = 0, \qquad (1)$$

where T is the temperature, x the coordinate, λ the thermal conductivity, c and ρ are respectively the heat capacity and density of the solid mixture of reactants, Q is the rate of evolution of the heat of reaction, and U is the rate of propagation of the thermal wave front.

However, there are fundamental differences between the process under consideration and combustion, which are reflected in the character of the dependence of Q on the variable: Q is a function not of temperature but of its derivative with respect to the coordinate. We express Q as a function varying abruptly from 0 to Q^* at $dT/dx = (dT/dx)^*$, this value remaining unaltered throughout a specific time interval τ. Physically, this implies that the heat evolution in the reaction starts only in response to the brittle breakdown of the specimen under the influence of thermal stresses attaining the ultimate strength of the material. The use of the quantity τ as the parameter of the reaction time reflects both features of the hypothesis being developed, according to which the period when the chemical reactivity is maintained in the course of the formation of a crack is limited by the operation of a deactivation process (for example, as a consequence of the recombination of active species on the surface of the break). When applied to the stationary model considered here, described by Eqn. (1), the parameter τ contains information about the reaction zone (the dispersion zone) in the running front whose size is $U\tau$. At each point within this zone, the reaction takes place at a rate Q^*, while outside its limits its rate is $Q = 0$.

The boundary conditions are formulated in the following form:

$$T|_{x=-\infty} = T_0, \; T|_{x=+\infty} = T_0 + Q\tau/c\rho \equiv T_{max},$$

where T_0 is the initial temperature of the specimen and T_{max} the maximum temperature of the adiabatic heating of the specimen. The model is assumed to be quasi-homogeneous, i.e. it is postulated that the characteristic size of the grain formed in the dispersion zone is much smaller than the width of the temperature wave front.

Eqn. (1), where the heat source is represented by a function of the type indicated, can be integrated in an analytical form when account is taken of the boundary conditions presented above and has a solution in the form of a running wave. We shall concentrate attention on the analysis of the dependence of the rate of propagation of the reaction wave on the parameters. This dependence assumes the following form:

$$g(u) \equiv \{1 - \exp(-u^2)\}u^{-1} = G, \qquad (2)$$

where $u = U(\tau/a)^{0.5}$ is the dimensionless velocity of the travelling wave (the parameter to be determined), $G = (dT/dx)^*(a\tau)^{0.5}/(T_{max} - T_0)$ is the specified dimensionless critical temperature gradient, and $a = \lambda/c\rho$ is the thermal diffusivity.

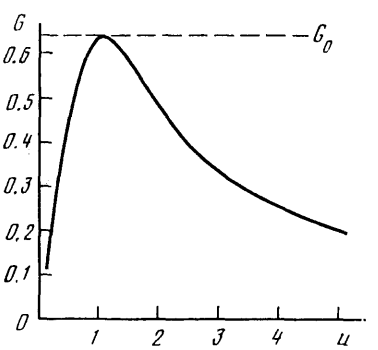


Figure 4. Dependence of the critical temperature gradient on the rate of propagation of the reaction wave.

Fig. 4 shows that an autowave solution of Eqn. (2) exists only for $G < G_0 \simeq 0.64$. Physically, this implies that, in the system described by the given model, the autowave regime in the propagation of the reaction in the solid mixture of reactants becomes impossible when the material of the specimen is strengthened to a definite extent, when the heat and rate of reaction are reduced, and also when the thermal diffusivity of the system is increased.

An important feature of Eqn. (1) is the non-unique nature of its solution. In the region $G < G_0$, two values of the stationary velocity of the running wave correspond to one value of the parameter g. We shall compare the characteristics of both regimes of the wave process. To simplify the treatment, we shall go over to the region $G \ll G_0$ in which Eqn. (2) is soluble for u. The expression for u, corresponding to the regime with a low velocity (the "slow" wave regime), has the form

$$u = a(dT/dx)^*/(T_{max} - T_0) \text{ or } u = a(dT/dx)^*/(Q^*\tau/c\rho), \quad (3)$$

while the expression corresponding to a high velocity (the "fast" wave regime) is

$$u = (T_{max} - T_0)/(dT/dx)^*\tau \text{ or } u = (Q^*/c\rho)/(dT/dx)^* \quad (4)$$

When the process takes place in the "slow" wave regime, it is possible to see features which reflect the similarity of this process, despite the differences in its physical nature, to the classical combustion process: the velocity of the wave depends on the thermal diffusivity in the same way as in the propagation of a flame; the position of the reaction zone in the wave front is the same as in combustion, i.e. it is located near the point of the maximum temperature T_{max} [the critical gradient $(dT/dx)^*$, for which the reaction is initiated, is in fact located near T_{max}]; most of the temperature profile of the front corresponds to the inert heating of the specimen (the zone referred to as the "Michelson" zone in the theory of combustion).

The characteristics of the process in the "fast" wave regime are significantly different. The most striking feature is the absence from Eqn. (4) of the dependence of the rate on the thermal diffusivity. The physical explanation of this result, which is unexpected for a problem with conductive heat transfer, is associated with the characteristic features of the structure of the "fast" wave front. In this case, the temperature profile of the wave front is much steeper than in the low velocity regime and the coordinate of the onset of reaction is located in the leading part of the front near T_0. This in fact explains the disappearance of the influence of the parameter a on the wave process, because the temperature gradients are high and close to the critical value even in the unheated part of the front. In terms of qualitative features, the "fast" wave regime is close to that observed experimentally.

In order to test the agreement between the experimentally observed phenomenon and the phenomenon considered in theoretical terms, it is of fundamental importance to attempt to realise experimentally the "slow" wave regime.

It was initiated (in conformity with theory) not by pulsed heating but by slow heating of the initiation zone. In special experiments,[18,22] the specimen was placed in a cryostat in boiling nitrogen vapour. Under these conditions, it was possible to observe, together with the "fast" wave (whose velocity did not differ from that described previously), also a "slow" wave (Fig. 5). Evidently the velocity of the "slow" wave is approximately an order of magnitude less than that of the "fast" wave, which agrees with data calculated by Eqns. (3) and (4).

It is noteworthy that the practical achievement of the "slow" wave involved certain difficulties. Initiation by slow local heating did not induce the appearance of a slowly propagated wave in each experiment. The "fast" wave was frequently initiated. Cases were observed where the "slow" wave generated was converted into the "fast" wave during its movement. This result is a consequence of the instability of the "slow" wave regime.

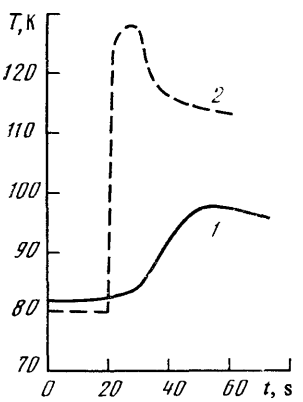


Figure 5. Time scan of the temperature profiles of the $C_4H_9Cl + Cl_2$ reaction propagation waves on slow (curve *1*) and rapid (curve *2*) heating; *1*, $U = 1$ mm s^{-1}; *2*, $U = 12$ mm s^{-1}.[18]

VI. Autowave reactions under the conditions of uniform compression and the role of mechanical stress dynamics

It follows from the above analysis that the effect of various factors on the strength characteristics of a solid mixture of reactants can serve as an instrument for testing the ideas being developed. For this purpose, studies were made of the influence of high pressures on the dynamic characteristics of autowave reactions[19] and also of the role of the rate of application of a stress and of the regimes in the cracking of the specimen on the excitation of reaction by a mechanical influence.[33]

In conformity with the theoretical prediction,[18] an increase in the pressure applied to the specimen reduced the velocity of the reaction wave front. The decrease in velocity at a pressure of 6×10^8 Pa proved to be very considerable—approximately by a factor of 2.5–3 compared with the rate of the process in the non-compressed specimen. Thus the increase in the homogeneity and structural order in the matrix under the influence of pressure, leading to its strengthening and hindering the formation of cracks, slows down the dispersion-reaction travelling wave, which is associated, according to Eqn. (4), with the increase in the critical value of the temperature gradient $(dT/dx)^*$ leading to the brittle breakdown of the specimen.

Experiments undertaken to investigate the role of the dynamics of the application of a mechanical stress, which determine the brittle or plastic character of the breakdown, were performed with film specimens 50–100 μm thick prepared from a chlorine–butyl chloride mixture. Impact by a striker (regime involving the rapid application of a stress, pressure $\sim 10^8$ Pa, duration of impact ~ 0.1 s) leads to the appearance of a network of cracks. Such treatment of

an irradiated film, inducing brittle breakdown, also induces an autowave.

On local impact by a striker in the regime involving a slow application of a stress to a film subjected to the same dose of γ-radiation, a chemical reaction is not initiated although an appreciable trace remains on the film in the form of a plastically deformed imprint having the shape of the cross-section of the striker.

Thus neither a significant plastic deformation (both on uniform compression and on local shearing) of the solid reaction systems investigated nor their transition to a highly stressed state under the influence of a static load are factors responsible for the critical phenomena and autowave processes observed in the reactions of these systems. A series of experiments[19,33] provided new important evidence for the decisive role of brittle breakdown in the mechanism of the phenomena under consideration (for further details, see Barelko et al.[27]).

VII. Expansion of the range of systems investigated (new types of autowave process)

Studies have demonstrated the wide occurrence of autowave phenomena in cryochemical reactions of solids and the identity of their physical mechanisms in a wide range of chemical systems. This justified the hypothesis that autowave reaction regimes can prove useful for the creation of new non-traditional chemical technologies. In the autowave processes described above, the principal technological problems (activation of the chemical system, supply of energy, and mixing of the reactants) are solved by combined procedures involving the use of the energy of the chemical reaction. The high rates of the chemical reaction occurring at low temperatures in the autowave regime are also extremely attractive. All this has stimulated the search for new objects of study.

1. Waves in acetaldehyde

In the light of the foregoing, the study of the post-polymerisation of γ-radiolysed solid acetaldehyde was extremely interesting. The kinetics of this reaction had been studied previously by an integral calorimetric method.[34] However, the development of ideas about autowave processes made it necessary to return to the analysis of the characteristics of the given reaction at a new qualitative level. This system is of special interest in connection with two factors. Firstly, the observation of the autowave regime in the polymerisation of acetaldehyde would provide the first example of a cryochemical wave in a one-component system. Secondly, the above reaction is characterised by a heat change smaller almost by an order of magnitude than in the systems studied previously. This created a basis for a more detailed specification of ideas concerning the role of the isothermal and non-isothermal mechanisms and about their interaction in an autowave process.

The propagation of the polymerisation front in solid radiolysed acetaldehyde at the relatively high temperatures 117–147 K (close to the melting point of the monomer which is 150 K) had been observed long before our investigations and had been recorded by thermographic measurements and cinefilming.[35]

This phenomenon was interpreted[35] within the framework of the classical thermal mechanism of combustion. Having restricted their treatment to one thermal conductivity equation and having made a number of assumptions, the authors obtained an extremely short time for the addition of one monomer unit to the polymer chain ($\sim 10^{-8}$ s). Subsequently, the kinetics of this reaction were studied in detail by the calorimetric method in the slow scanning regime with respect to temperature and directly in the field of the specimen.[34] The time required for the addition of one monomer was only $10^{-1}-10^{-2}$ s. The problem of the legitimacy of the application by Psheshezhetskii and Tupikov of the theory of combustion to the description of the layer-by-layer propagation of the polymerisation front naturally arose in this connection.

The principal ideas concerning the mechanochemical feedback in an autowave process were confirmed in the study of this system. An autowave polymerisation regime occurred in polycrystalline acetaldehyde already at 4.2–77 K and its principal characteristics were investigated.[36] The polymerisation wave in crystalline acetaldehyde was observed in massive (cylindrical) and thin-film specimens in both nitrogen (77 K) and helium (4.2 K) baths. The wave was excited in response to the local brittle breakdown of frozen aldehyde.

When the autowave passed through the specimen in the helium bath, the maximum temperature in the front did not exceed ~130 K, i.e. was significantly lower than the melting point of the monomer (150 K). Consequently this system provides an example of an autowave process occurring exclusively in the solid phase. This is in fact why conditions were created for the analysis of the changes in the structure and phase state of the polycrystalline specimen induced by the passage of the mechanochemical cryowave through it. According to the ideas being developed, the chemical reaction front consists of a mechanical dispersion zone moving in the solid reactant. Examination of the cinegrams recording the passage of the wave established that behind the front the initially opaque polycrystalline specimen is fully clarified. It could be assumed that this clarification is associated with the amorphisation of the specimen.

This hypothesis was tested by calorimetric analysis which made it possible to determine the ratio of the amorphous and vitreous phases in the solid matrix from the change in the heat of fusion. In order to carry out such analysis, the acetaldehyde specimen was transferred to a bath of liquid nitrogen after an autowave had passed through it in liquid helium and was then sliced into several parts along the height of the cylinder. Each part was placed in a calorimeter at 77 K and the calorimetric heating curve was recorded for it. It was found that, after the passage of the wave, the specimen contained no crystalline phase along its height (only a heat capacity jump accompanying devitrification was detected in the calorimetric experiments and a signal corresponding to the heat of fusion was absent). On the other hand, when the process was carried out not in the autowave regime but in the regime involving the slow heating of the entire specimen in the calorimeter (without the brittle breakdown initiating the autowave), the unreacted monomer retained its crystallinity. Thus the passage of the mechanochemical wave through the polycrystalline specimen results in its amorphisation, for which two factors are responsible: the formation as a result of the reaction of an amorphous polymer and the mechanical dispersion of the specimen in the front.

The rate of propagation of the autowave depends on the dose of the preliminary γ-irradiation. As in the system studied previously,[27] there is a critical dose necessary for the attainment of the autowave regime. The size of this dose increases with decrease in the thermostat temperature (Fig. 6). It could be postulated that the increase in the rate of propagation of the wave with increasing dose is caused by the increase in the concentration of stabilised active centres accumulated in the system during the preliminary radiolysis. However, the increase in the concentration of paramagnetic centres

(radical-ions and radicals) during the radiolysis at 77 K of polycrystalline acetaldehyde takes place linearly only up to a dose of ~50 kGy and then slows down. After the attainment of ~700 kGy, the accumulation of centres ceases altogether. On the other hand, the rate of propagation of the wave in this range continues to increase in proportion to the dose.

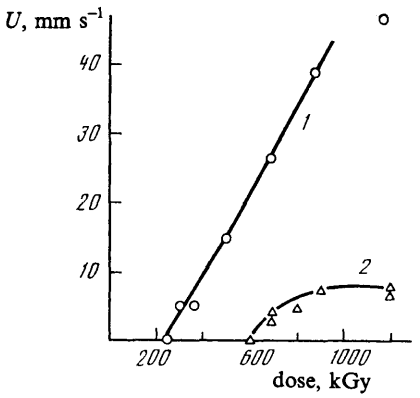


Figure 6. Dependence of the rate of propagation of the polymerisation wave front in polycrystalline acetaldehyde on the preliminary irradiation dose at 77 K (curve *1*) and 4.2 K (curve *2*).[36]

It is known that, in the low-temperature radiolysis of acetaldehyde in a matrix, its decomposition products appear—methane and carbon monoxide, which are in the condensed state at 77 K. When the polymerisation wave passes through the system, these radiolysis products are gasified (the boiling points of CH_4 and CO are respectively 111 and 81 K), which can facilitate the brittle breakdown of the specimen and can accelerate the movement of the running reaction front.

The problem of achieving the wave process in the vitreous acetaldehyde matrix is of great interest. Even on rapid cooling, pure acetaldehyde cannot be converted into the vitreous state[34] and its polymerisation in the vitreous state had not therefore been studied previously. Kichigina et al.[37] investigated a vitreous solid solution of acetaldehyde in butyl chloride (BC), in which local brittle breakdown induced an autowave polymerisation regime. It was found that the critical dose of the preliminary γ-irradiation, above which the autowave propagation of the process in the vitreous solution can be attained, is only 60 kGy, while in crystalline acetaldehyde it exceeds 300 kGy.

Convincing evidence has also been obtained for the occurrence of polymerisation in this system via a cationic mechanism. On the other hand, in previous studies,[27] autowave regimes had been observed only in systems in which characteristic reactions are radical processes.

2. Autowaves of the detonation type

Experimental data indicating the explosive character of the reaction occurring in condensates of atomic magnesium with halogenohydrocarbons (the formation of organomagnesium compounds) and the polymerisation of cyclopentadiene with $TiCl_4$, initiated a 77 K by the impact of a metallic needle, have been published.[38,39] The authors of the above studies did not, however, investigate the dynamics of these processes and the characteristics of their development in time and space. The idea arose naturally that the above studies[38,39] were concerned with yet another type of autowave cryochemical reactions occurring under qualitatively new conditions and not requiring a preliminary activation of the solid matrix by γ-radiation. Furthermore, Kabanov et al.[39] drew attention to the wave character of the polymerisation process in a film and even estimated the velocity of the front (~200 mm s^{-1}).

We observed similar phenomena in experiments with non-irradiated thin-film ethylene + chlorine, propene + chlorine, and vinyl chloride + chlorine cocondensates.[23] It was possible to establish that the chlorination of these hydrocarbons at 77 K takes place not in the form of a homogeneous explosion but in an autowave regime and the film is pricked or scratched and is characterised by extremely intense dispersion in the front of the self-propagating reaction, which is indicated, in particular, by the "recoil" of finely dispersed fragments of the reacting matrix accompanying the wave. The second of the above factors as well as the high velocity of the front (tens of centimetres and even metres per second) give grounds for agreement with the authors,[39] who believe that yet another variety of a low-temperature wave, mechanochemical in nature and close in its essential physical features to detonation phenomena (admittedly with features of degeneracy—presonic velocities), may exist in a solid.

This problem is complex and requires the development of fundamentally new theoretical and experimental approaches to the elucidation of the mechanisms of the chemical reaction energy transfer in low-temperature detonation processes in solid systems.

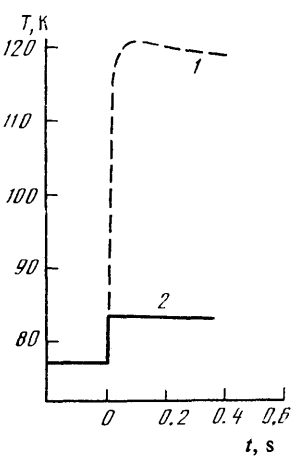


Figure 7. Temperature profiles of the reaction wave in radiolysed (curve *1*) and photolysed (curve *2*) $C_4H_9Cl + Cl_2$ specimens. The initial concentration of radicals was in both cases 2×10^{18} g^{-1}:[40] *1*, $U = 10$ mm s^{-1}; *2*, $U = 400$ mm s^{-1}.

Here one is dealing not with the usual mechanism of the excitation of the detonation wave, known in the classical theory of explosion, but with an unusual type of detonation which may be called gas-free detonation.

3. Autowaves in photoactivated systems

There exists yet another and apparently very wide and varied, as regards manifestations, class of solid systems which react at low temperatures in accordance with the travelling wave laws. Here we have in mind experiments on the local mechanical initiation of a reaction in photoactivated solid matrices.[40] It has been found that preliminary treatment of previously investigated solid systems, for example $C_4H_9Cl + Cl_2$, at 77 K not by γ-radiation but by light also leads to the accumulation in the matrix of potential energy, which can be used for the subsequent initiation of a specific chemical reaction with the aid of local mechanical breakdown. Under these conditions, the process occurs, as in the case of γ-irradiation, in the form of a layer-by-layer dispersion running wave accompanied by a chemical reaction. Furthermore, in the first experiments designed to investigate autowave reaction regimes in photolysed matrices, new features were discovered in addition to the usual features characteristic of the self-propagation of reactions in a solid at low temperatures.

We shall compare the principal characteristics of reaction autowaves in radiolysed and photolysed $C_4H_9Cl + Cl_2$ systems at 77 K (Fig. 7). In the front of a wave propagated in a photolysed specimen, there is no pre-explosive heat exchange, as in the radiolysed system. However, the remaining characteristics of the wave processes differ appreciably. Indeed the rate of propagation of the front in the photolysed system is significantly higher ($\sim$400 mm s^{-1}) than in a radiolysed system ($\sim$10 mm s^{-1}) for identical concentrations of the stabilised alkyl radicals.

The temperature profiles of the front also differ greatly: the maximum temperature in the radiolysed system is 121 K, while in the photolysed system it is only 83 K, i.e. in the latter case the superheating in the reaction zone relative to the thermostat reaches only $\sim$6 K. These differences are probably associated with the difference between the mechanisms of the chemical reactions occurring on mechanical breakdown. For the same initial concentrations of the alkyl radicals, the initial rate of reaction in the radiolysed system is slower than in the photolysed system, because some of the chlorine atoms propagating the chain are captured by Cl^- ions, which are not formed on photolysis.[41]

The problem of the vibrational instability of the movement of the cryoreaction front, demonstrated in relation to the pulsating character of the cryowave in the methylcyclohexane + chlorine system, has been formulated.[20] The hypothetical mechanism of this phenomenon was based on the fact that in the radiolysed system the zone corresponding to dispersion induced by the chemical reaction moves ahead abruptly (at rates of the order of the velocity of sound) to a depth comparable to the characteristic fragmentation grain size. The chemical reaction begins in this disrupted layer and a new jump of the reaction zone in space occurs only after the attainment of a critical density or temperature gradient. Since the rate of the chemical reaction in the breakdown zone of the photolysed system is higher, the necessary conditions for the next jump of the reaction zone are attained faster than in the radiolysed system, which in fact increases the average velocity of the wave.

One can also postulate that photolysis results in a more significant decrease than in the radiolysis by γ-rays, in the strength of the system and in the accumulation of metastable states in the latter, as a result of which the characteristic front velocities increase. One cannot rule out the possibility that the higher rates of the process in photolysed systems are also caused by the involvement of mechanisms of the detonation type.

4. The role of radicals and ions in solid-phase processes

We shall deal with yet another apparently very important aspect of the problem under consideration, which was considered by Barelko et al.[42] It is known that significant changes occurring in the lattice of the solid under the influence of the flux of radiation are not associated solely with the formation of stabilised radicals and ions. Appreciable energy changes occur in the matrix also as a result of its deformation and loosening. The deformation energy retained within the bulk of the solid can reach high values comparable to the solid–liquid and sometimes also solid–gas phase transition energies. One can apparently assume that in the irradiated solid there is a continuous spectrum of states whose energy band extends from the zero value (equilibrium state corresponding to an ideal crystal) to the energy corresponding to a free atom or fragment all the bonds of which with the lattice have been ruptured.

Thus one cannot rule out the possible activating role of this accumulated energy in the chemical process. Indeed, in the autowave reaction regimes described above, a pronounced non-linear relation was observed between the potential chemical reactivity (velocity of the wave) and the concentration of the stabilised active centres of the radical type. The most striking result of this kind was obtained in a study of the dependence of the rates of the layer-by-layer propagation of the polymerisation wave in solid acetaldehyde on the concentration of the radicals stabilised on radiolysis.[37] For doses in excess of the critical value ($\sim$300 kGy), local excitation initiates the reaction wave, whose velocity depends linearly on the dose throughout the experimental range (Fig. 8*a*). On the other hand, measurement of the EPR signal of the specimen indicates a significant deviation of the concentration of the radicals from the linear law even for doses of $\sim$50 kGy (this can be seen particularly convincingly in Fig. 8*b*). Consequently the potential chemical reactivity of the irradiated solid matrix, whose quantitative measure is the velocity of the autowave, is not determined solely by the concentration of the stabilised radicals.

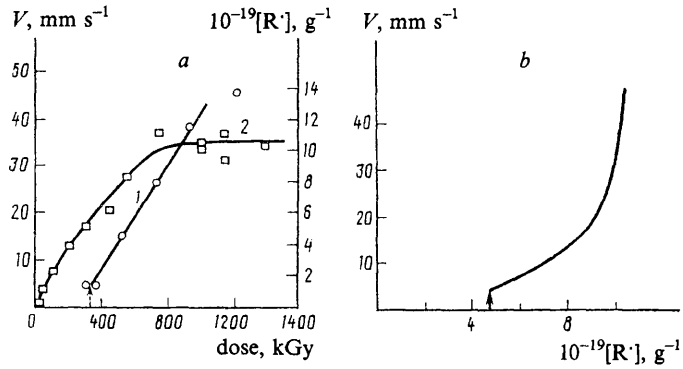


Figure 8. Dependence of the velocity of the polymerisation wave front (curve *1*) and of the rate of accumulation of radicals (curve *2*) in crystalline acetaldehyde on the γ-irradiation dose at 77 K (*a*) and the dependence of the velocity of the wave on the radical concentration (*b*) obtained from curves *1* and *2*.[37]

Direct experimental evidence has been obtained[43] for the amorphisation of crystalline methanol during its radiolysis. Direct calorimetric measurements during the heating of the specimen radiolysed at 77 K made it possible to detect heat evolution

associated with the crystallisation of the amorphised methanol. Calculation showed that the energy stored on irradiation, whose carrier is the metastable amorphous phase formed, exceeds appreciably the part of the energy accumulated in the radical and ionic states.

VIII. Conclusion

In conclusion of the description of the relevant data, it is important to define the place occupied by the phenomena considered here in the general series of different self-propagating chemical processes. For this purpose, we shall attempt to classify the chemical systems characterised by autowave phenomena. Without going into details, we shall differentiate in terms of phenomenological features two large groups to which virtually any of the systems of this kind known at present can be assigned: (1) processes of the type of combustion (the factor determining the existence of the running wave regime in this case is thermal non-linearity) and (2) processes of the branched-chain type (the so-called "chain combustion" associated with kinetic non-linearity of an autocatalytic character). Evidently the mechanism of the self-activation of a frozen reactive system, which determines the characteristic features of the wave processes investigated, is in essence close to the branched-chain mechanism.

The concept of the branched-chain mechanism in solid state chemistry is itself by no means new and has been discussed in the literature for many decades.[44,45] It is constructed on the basis of the claim that the active centres ("nuclei") of the reaction are all kinds of defects distributed in the solid matrix of the reactants and progressively multiplying in it when acted upon by the influences induced in the solid by the reaction itself. The operation of this mechanism has been examined in greatest detail and most convincingly in a large series of investigations[46–50] of the thermal decomposition of ammonium perchlorate at temperatures of about 500 K.

The authors of these studies, who observed the changes in the structure of a decomposing crystalline specimen, established that (1) the reaction of the solid reactant takes place within the framework of the strong influence on the process by the mechanical stresses induced by the decomposition reaction and consists of stages involving the formation and growth of the reaction "nuclei", their multiplication, the increase in their density, and their coalescence and (2) that, on coalescence of the separately developing reaction zones, a single reaction front may be formed and can move within the specimen in the form of a cloud of multiplying nuclei at low but quite definite velocities (of the order of 10^{-4} mm s^{-1}).

Critical phenomena, which are known to constitute a necessary feature of branched-chain and autowave processes, were not observed in the above studies.[46–50] This is most probably due to the retention in the perchlorate decomposition reaction of the leading role by the thermal mechanism. This is in fact indicated by the pronounced exponential dependence of the overall rate of decomposition of the salt (as well as of the velocity of the front) on temperature: on cooling, the reaction rapidly slows down and ceases almost completely already at 460–470 K. One should add that the perchlorate decomposition reaction is not strictly a solid-phase reaction, because it is accompanied by a change in the phase state. The authors[46–50] in fact see in this feature (in the formation of gaseous decomposition products) the cause of the mechanical deformation of the solid reactant matrix and of the development in the latter of defects activating the reaction.

Several years ago, the concept examined above was extended to low-temperature solid state chemistry.[51] The authors[51] used the idea of the self-activation of the matrix due to the feedback between the chemical reaction and the stressed state of the frozen specimen comprising the reactants to explain and describe the so-called "explosion on cooling" which they observed in the photolysed $CH_3C_6H_{11} + Cl_2$ system. The model proposed[51–53] is unfortunately not entirely concrete, because it operates with an abstract quantity called by the author the "excess free energy of internal stresses". No methods were proposed in the above studies for its measurement or for the estimation of its numerical values. Nor is the relation between this characteristic and the defectiveness of the solid matrix discussed. Furthermore, in order to achieve the feedback, the authors had to introduce into the model the feed balance equation, although their claims are based on non-thermal ideas about the mechanism of the self-activation of the reactants at low temperatures. Nevertheless, the essential features of their ideas[51–53] can be formulated by the following phenomenological postulate: the mechanical energy accumulating in the matrix promotes directly the acceleration of the chemical solid-phase reaction by the corresponding reduction of its activation barrier. In other words, in contrast to the molecular tunnelling mechanism,[4] the proposed model of low-temperature reactions in a solid is constructed wholly within the framework of the classical Arrhenius kinetics supplemented merely by certain elements of the kinetic theory of mechanical strength.[54]

We shall attempt to estimate the reality of this model. For this purpose, we turn to the results of our studies of cryochemical solid-phase reactions carried out under the conditions of the artificial transition of the specimen to a highly stressed state (see Section VI). To make the system concrete, we shall deal with the same hydrocarbon chlorination reaction which was investigated in the above studies[51–53] but with preliminary activation by γ-irradiation and not by light. It has been established experimentally that application of a mechanical stress to the specimen under the conditions of uniform compression up to pressures $P = 6 - 10^8$ Pa not only does not promote the reaction but actually hinders it: the reaction does not occur in a matrix in a highly stressed state, while the rate of the autowave process in the compressed specimen is appreciably reduced. Estimation of the specific energy introduced into the specimen yields $\Delta U = P^2/E \simeq 6-12$ kJ mol^{-1}, where E is the modulus of elasticity amounting to $(3-6) \times 10^9$ Pa, according to Benderskii et al.,[55] at low temperatures for this vitreous systems investigated. This value of $\Delta\mu$ is fully comparable to the activation energies for the test reactions measured previously[28] (~ 20 kJ mol^{-1}) and it should seemingly reduce significantly the activation barrier and accelerate and not inhibit the reaction. Naturally, the above considerations are far from sufficient to reject the concept developed by Benderskii and co-workers.[51–53] However, they throw doubt on the very idea that the mechanical energy of the deformed solid matrix can participate directly in its chemical activation.

Having concentrated in their investigations on the study of critical effects, Benderskii and co-workers[51–53] confined themselves to considering uniform quasi-homogeneous models in the zero-dimensional approximation. Problems concerning the extent to which the onset of the reaction in the specimen is synchronous and the mechanisms of the transfer of the excitation of the chemical reactivity within the bulk of the reacting solid, which are of fundamental importance, were only touched upon in the above

studies,[51–53] while the question of the existence of autowave regimes remained almost fully outside the framework of these investigations.‡

The ideas which we have developed concerning the nature of autowave highly intense regimes in a cryochemical reaction are constructed on the basis of a mechanism, which can be called, by analogy with the mechanism already mentioned,[8] an "energy chain". It follows from the data presented in this review that this analogy is entirely justified because the proposed mechanism involves a chain of stages, closed by negative feedback and accompanied by the transformation of the energy of the chemical reaction in time and space. Indeed, it is suggested that during the reaction part of the energy evolved accumulates in the solid matrix in the form of an elastic deformation, i.e. the unreacted part of the specimen passes in this stage to a mechanically non-equilibrium and in a certain sense "excited" state; the potential energy of this metastable state is then transformed into chemical energy. However, the transformation is not direct but occurs only through the brittle breakdown stage in which conditions are created for the chemical reaction, occurring on freshly cleaved surfaces or near them where the energy has been concentrated. This mechanism in fact determines the self-maintaining regime in the reaction of a solid specimen excited by layer-by-layer autodispersion. Ideas postulating the branched-chain character of the process are reflected by the pattern of the continually branching and migrating network of cracks in the reacting matrix.

The operation of this mechanism of the recovery of the energy of the chemical reaction, leading to the self-activation of the solid matrix, is especially favoured by low and ultra-low temperatures. Under these conditions, where the dissipation of the energy stored in the mechanically non-equilibrium matrix is retarded (as a consequence of the limiting constraint on the molecular mobility and the virtually complete loss of plasticity), there is in fact the possibility of an extremely large accumulation of energy in the lattice. The liberation of this energy on mechanical breakdown ensures the subsequent development of the self-maintaining reaction of the reactants.

In the study of solid-phase chemical reactions under the conditions of high pressures combined with shear forces, an "ultrahigh" molecular mobility was observed.[56] In order to interpret such chemical processes, the authors[56] had to postulate the existence of diffusion coefficients exceeding by 10–15 orders of magnitude the usual values. It is to be expected that the autowave ideas, based on allowance for the self-dispersion of the reacting matrix, will prove useful for the explanation of these surprising phenomena.

The postulates being developed must be resorted to also in order to account for the processes involving the "cold" evolution of matter in the universe. In particular, one can imagine a process in which compounds such as ammonia and methane are formed from a frozen mixture of the elements. Such compounds have been detected in appreciable amounts in the solid state on the cold planets of the solar system. The diurnal changes in temperature and the thermal stresses arising under these conditions in the solid coating of the planet might have served as the instrument for continuous mechanism breakdown leading to the chemical bonding of the components which were additionally activated by solar radiation. The next stage of evolution, in which solid ammonia and hydrocarbons, dispersed in the "solar mill", are converted into the simplest amines, also appears likely. It is to be expected that a direct experimental test of the chain of cryosyntheses described here will be an important step in the understanding of many secrets of space chemistry.

The importance of the results of studies on autowave phenomena examined in this review may go beyond the framework of the low-temperature field alone. It may be that the exceptionally high rates of reaction frequently observed experimentally in systems of different chemical nature are in fact associated with the autodispersion of a solid reactant matrix—a process which transfers the chemical reaction from the bulk phase to the highly reactive cleavage surface. These rates may be comparable to or exceed greatly the rates of the corresponding processes in liquid media and special attention should therefore be devoted to the non-thermal, non-equilibrium mechanisms of the activation of a solid matrix due to the inclusion in the chemical process of the energy accumulated by the lattice. A specific example illustrating this general consideration is provided by a study[57] in which the self-activating role of the dispersion of the particles of a refractory component was considered in the formation of intermetallic compounds from powders in a completely different temperature range. In this system, the dispersion of the solid component is referred to as the wetting of the particles by the liquid reaction products (a kind of mechanochemical autocatalysis).

The problem of the legitimacy of the quasi-uniform ideas, very widely used in solid-phase cryochemical kinetics, which rule out from consideration matter and energy transfer processes within the bulk of a solid matrix, was touched upon in the Introduction. The ideas described in this review concerning the autowave dynamics of reactions of solid reactants, the sensitivity of the process to local perturbations, and the non-uniformity of the development of the reaction in the specimen intensify doubts about the applicability of the above classical approach to the kinetics of solid-phase reactions. Under conditions where non-linear mechanisms operate, which are particularly characteristic of solid state chemistry, a spatially uniform course of the process is extremely unlikely. As a result of this, the integral signal due to the chemical reaction (and this signal has in fact been recorded in the vast majority of studies on the kinetics of solid-phase reactions) represents a superposition of signals arising from different points within the specimens and differing both as regards rate and phase. Evidently such a signal cannot carry reliable information about the true process kinetics and the attempt to correlate it with theoretical kinetic models described by a system of ordinary different equations would be simply erroneous.

‡ In addition to the above considerations, we should like to draw attention to an important methodological factor which might have escaped the attention of Benderskii and co-workers.[51–53] This concerns the influence of the material of the cells on the conditions in the initiation of the photochemical reaction. When experiments are carried out in γ-irradiated or photolysed systems, cooling of the specimen can, as already stated above, induce a rapid reaction. However, a decisive factor was not cooling as such but the rate of decrease of temperature. By reducing the rate of cooling, it was easy to maintain the specimen in a fully inert state down to 4.2 K. However, this is characteristic only of Pyrex bulbs. Another picture is observed when quartz bulbs are used. The strict reproducibility of "explosion on cooling"[51–53] might have been associated with the exclusive use of quartz cells in the experiments. The coefficients of the thermal deformation of this material differs greatly (in contrast to that of ordinary glass) from that of the reactants, as a result of which the inevitable peeling of the substance from the walls of the bulb on cooling (i.e. fracture) induced the "explosion" described by Benderskii and co-workers.[51–53]

We shall now turn, as an example, to the case of "polychronic" kinetics well known in solid-phase radiation chemistry.[58] In order to explain the phenomenon of the "kinetic arrest of the reaction", actually recorded with the aid of integral methods, a spectrum of kinetic constants is introduced. Its presence is attributed to the non-uniformity with respect to energy states of the active centres distributed in the matrix. The autowave approach makes it possible to explain the experimental phenomenon without resorting to a polychronic kinetic scheme: it is easy to image that separate reaction waves arise on local perturbations during the process and are propagated frontally throughout the specimen, being arrested at some kind of non-uniformities of the matrix or its macrodefects. Another situation, where the chemical process simply cannot develop uniformly because of spatial instability and the reaction is accompanied by the formation of the so-called "dissipative domain structures",[59] is also entirely realistic.§ Thus in each specific case, quasi-uniform models and in particular "polychronic" kinetic models require special experimental justification, which rules out the influence of autowave phenomena on the dynamics of the development of the reaction.

The ideas about the activating role of self-disruption may prove useful in a number of related fields of study dealing with solids.

This may in fact be a clue to the high sensitivity of many explosive substances to friction and impact. Hitherto the general theory of the sensitivity of explosive substances to mechanical influences has been constructed solely on the basis of thermal ideas, according to which the mechanical energy introduced into the specimen must be transformed initially into thermal energy to create a hot spot, and only then can it excite explosion via a "centre of origin" mechanism. It appears likely that the initiation of an explosive reaction is caused not by the conversion of mechanical energy into thermal energy but by the appearance in the specimen of chemically high reactive cleavage planes arising on friction or impact.¶

The processes involving the transition of a solid from a metastable, amorphous state to a polycrystalline state, which have been vigorously investigated (especially in recent years) (see Shklovskii[64] and the references therein) are autowave in character and outwardly resemble the solid-phase cryochemical reactions considered in this review. In this class of processes, one cannot rule out the operation of the same autodispersion mechanism, facilitating the phase transformation as a result of its transfer from the bulk phase to the fracture surface. Indeed, both classes of processes resemble one another as regards their essential physical features and are associated with the rearrangement of the solid matrix. Both are exothermic and differ only in the magnitude of the thermal effect. Furthermore, one should add that the cracking and dispersion of the specimens, which can be observed even with the naked eye, are extremely typical for wave processes involving the decomposition of amorphous states.†

Yet another field, seemingly very remote from solid state chemistry, is that concerned with the puncturing of transparent media by a flux of radiant energy with a high power (radiant breakdown).[66] As regards their character, these processes can also be classified as autowave processes. The current theory describing these processes, is close in its essential features to the theory of combustion. The difference consists solely in the transition from the exponential temperature variation of the intensity of the chemical heat evolution in the case of combustion to the exponential absorption of radiant energy by the solid medium in the optical breakdown. Analysis of the literature on the optical strength of glasses suggested the idea that the mechanism of the autoacceleration which we have developed in relation to chemical reactions in a solid can be resorted to also in order to describe the dynamics of the radiant disruption of glasses. Using these ideas, the picture illustrating the disruption of the specimen by a light flux can be represented as follows. The light-absorbing submicron impurities, always present in glasses, are heated by the radiant flux. The temperature attained under these conditions presents no risk to the material because of the intense conductive removal of heat from a given small centre and the heated zone, around the impurity particle, is just as small as the absorbing centre itself. However, owing to the high curvature of the spherical centre of such size, the temperature gradients generated are very high. This factor in fact influences the strength of the material and leads to cleavage and the peeling of the particles from the matrix. The non-equilibrium states on the cleavage plane arising at the instant of fracture begin to absorb energy vigorously, which leads to the heating of a fresh surface and then to the cracking of the next layer of the irradiated transparent medium. The cracking at the impurity can be initiated in this way with subsequent wave propagation of the disruption under the conditions of the layer-by-layer dispersion of the specimen. This process can be described theoretically with the aid of a phenomenological model completely identical with the model examined in the present review. The information published[66] about two regimes in the cracking of glasses, occurring as a function of the initial excitation conditions, is qualitatively predicted by the model indicated. The considerations described here concerning the mechanism of the optical breakdown of transparent media are apparently convincing, as shown, in particular, by their use of specialists in the given field.[67]

In conclusion of the review of studies on the phenomena involving the running waves of cryochemical reactions in a solid and of the analysis of the mechanisms controlling these processes, we may note that the studies which have been carried out are mainly phenomenological in character. Naturally, the next task is the solution of a whole series of fundamentally important problems associated with the elementary stages of the process. The main ones are the elucidation of the nature of the active states arising on the cleavage planes, their lifetimes, the establishment of the mechanism of the intensification of transport processes on fresh fracture

§ Similar phenomenon have been observed in heterogeneous catalysis,[60-62] in the field close to solid state chemistry.

¶ V V Boldyrev drew our attention to the fact that similar ideas concerning the nature of the sensitivity of explosives to friction and impact were put forward more than 30 years ago by Ubbelohde.[63] However, owing to the lack at that time of adequate physical justification, this concept was not developed further and was in essence forgotten.

† Yet another possible application of the ideas about self-maintaining phase transitions in a solid, formulated in a brief communication by American geophysicists, is extremely interesting.[65] They put forward a hypothesis according to which the phase transformations in terrestrial rocks as a result of the operation in them of an autocatalytic self-disruption mechanism are the main cause of earthquakes and other catastrophic geotectonic processes.

surfaces, the search for electrical signals associated with the emission of charged particles during the cracking process, and also the search for signals of the type of triboluminescence arising from the front of the dispersion (chemical reaction) running wave.

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The structure and properties of complexes simulating molecular recognition

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ABSTRACT. The main trends in the evolution of the concept of molecular recognition are examined. The possibility of using thermodynamic parameters for a quantitative characterisation of recognition and the effect of their relationships on the degree of recognition are analysed. Complexes, containing one or more hydrogen bonds, between macrocyclic compounds and metal ions, alkyl and alkylammonium derivatives, and various anions are characterised in detail as model compounds. The problem of competitive complexation in an aqueous medium is discussed. The role of computer-aided simulation of molecular recognition in applied studies relating to the design of biologically active compounds is assessed. The suitability of such a combination of experimental and theoretical studies, in which the models for molecular recognition could be constantly improved, is noted.

Contents

I. Introduction 219
II. Thermodynamics of molecular recognition 219
III. Complexes with hydrogen bonding 221
IV. Synthetic macrocyclic biomimetics 224
V. Simulation of equilibria in aqueous solution 227
VI. Computer-aided molecular simulation 229

I. Introduction

The phenomenon of molecular recognition may be regarded as fundamental for many biological processes—in the functioning of the immune system, the formation of substrate–enzyme and hormone–receptor complexes, the transmission of nerve impulses, and in the sense of taste and smell, etc.[1] Identification of the mechanism and nature of the interactions between the molecules in such systems is not only a fundamentally important scientific development but also should assist in the creation of a firm basis for resolving the extremely urgent applied tasks of obtaining specific biologically active compounds with pesticidal and pharmacological action.[2–4] It is obvious therefore that research workers have given very considerable attention to the problem of molecular recognition; the exponential rise in the number of publications on this topic in recent decades is an indication of this.

A considerable contribution to this scientific development has been made by the following Nobel prize-winners: E Fischer (the complementarity principle of substrate–receptor complexes), P Ehrlich (the "lock and key" mechanism in the action of the immune system), C Landsteiner (the specificity of serological reactions), L Pauling (establishment of the cooperation effect of weak forces, including van der Waals forces, electrostatic interactions, and hydrogen bonding between complementary structures), F H C Crick and J D Watson (the molecular structure of desoxyribonucleic acid), K Pedersen, J M Lehn, D Cram (the synthesis, structure, and properties of macromolecular polydentate ligands that can act as "hosts").

In the present review the task is to analyse the current trends in the development of the theory and experiment concerning the simulation of molecular recognition. The examination of material is carried out according to the order of complexity of the systems (from systems of several low molecular-weight compounds to complexes of ions and low molecular-weight compounds with synthetic macromolecular receptors and then natural molecular receptors). This type of presentation of the material is helpful for an assessment and analysis of the relative contributions of different noncovalent interactions to molecular recognition. It should be emphasised here that the degree of molecular recognition of chemical compounds increases by an order on going from a selective donor–acceptor interaction or hydrogen bonding of molecules, containing one electron-donor and one acceptor site, to selective complexation of metal ions with polydentate ligands, then to selective catalytic reactions, and finally to enzyme reactions.

The very large number of articles that have been devoted to molecular recognition make it necessary to leave out whole aspects of this topic from the present publication. However, the detailed reviews and books that have been published in recent years on the conformational analysis of macromolecules,[5–7] quantum-chemical calculations of biological systems,[8–10] and protein engineering[11] compensate for these omissions to a considerable extent. The classes of complexes reviewed have also been limited. Since the main focus of attention in this review is the nature of the noncovalent interactions in substrate–receptor systems, there is a detailed analysis of H-complexes, complexes of polydentate macrocyclic ligands, and mixed ternary complexes involving transition metal ions and aminocarboxylic and aminophosphonic acids.

II. Thermodynamics of molecular recognition

In considering the binding of a physiologically active compound A to a receptor R, the resulting concentration of complex AR can be given by the relationship†

$$[AR] = \frac{K_A [A] R_T}{1 + K_A [A]},$$

† R H Davies *Int. J. Quantum. Chem., Quantum Biol. Symp.*, 1987, (14) 221.

where K_A is the binding constant and R_T is the total number of molecules of receptor. The observed response E of the system to the introduction of compound A into it is a given function of the concentration of complex AR. In this case two possible relationships linking the binding [AR] with the observed response can occur. Thus, if the response is given by the equation

$$E = \frac{K_E\,[\mathrm{AR}]}{1 + K_E\,[\mathrm{AR}]},$$

where K_E is a given factor, when

$$E = \frac{K_A\,[\mathrm{A}]\,\tau}{1 + (\tau + 1)\,K_A\,[\mathrm{A}]},$$

where $\tau = K_E R_T$, or

$$E = \varepsilon\,\frac{K_A'\,[\mathrm{A}]}{1 + K_A'\,[\mathrm{A}]},$$

where $\varepsilon = \tau/(\tau + 1)$ and $K_A' = (\tau + 1)K_A$. Thus the three parameters—the binding constant K_A, the factor K_E, and the total number of molecules of receptor R_T—determine the recognitive and effector functions of a physiologically active compound A in its effect on a receptor.

The thermodynamic criteria of molecular recognition during competitive complexation in multicomponent solutions have been clearly stated in two articles.[12,13] A recognizer A_0 must bind with molecules of a particular type B_0, namely, with the correct effector, in a solution that contains N types of molecules (B_0, B_1, $B_2 \ldots B_{N-1}$) at a random series of concentrations. The probability of all the false recognitions can be denoted as P_f. Thus, the degree of recognition can be characterised by the number N of possible effectors amongst which A_0 correctly recognises B_0 and by the probability P_f of a false recognition.

For the simplest example—complexation between A_0 and B_i in the ratio 1 : 1—we obtain

$$\mathrm{A_0} + \mathrm{B}_i = \mathrm{A_0B}_i,$$
$$[\mathrm{A_0B}_i]/[\mathrm{A_0}]\,[\mathrm{B}_i] = K_{0i} = \exp\,(-\Delta G_{0i}/RT),$$
$$i = 0,\ 1,\ 2,\ \ldots\ N-1.$$

The probability in this case of a false recognition is equal to:

$$P_f = \frac{\sum_{i=1}^{N-1} [\mathrm{A_0B}_i]}{[\mathrm{A_0B_0}] + \sum_{i=1}^{N-1} [\mathrm{A_0B}_i]} = \frac{\sum_{i=1}^{N-1} [\mathrm{B}_i]\,K_{0i}}{[\mathrm{B_0}]\,K_{00} + \sum_{i=1}^{N-1} [\mathrm{B}_i]\,K_{0i}}$$

Hence there will be a greater degree of recognition the higher the ratio of the binding constant for correct recognition to that for false recognitions, namely, the greater the difference in free energies ($\Delta\Delta G$) which represents the difference between the concentrations of A_0B_0 and A_0B_i. The degree of recognition decreases, and hence the value of P_f increases, if the total number of molecules B_i, and B_0 in particular, is comparable to or less than the number of molecules of recogniser A_0. If the number of molecules A_0 exceeds the total number of molecules B_i and all constants K_{0i} are of a single order, virtually all of the molecules B_i will be bound in complexes A_0B_i and P_f will reach a value equal to unity.

Thus, highly specific recognition requires a large value of $\Delta\Delta G$, characterising the clearly defined capacity of the recogniser A_0 to interact with the correct (B_0) as opposed to false (B_i) effector.

It is evident from the description above that in order to develop quantitative models of molecular recognition, it is necessary to have information about the interactive capacity of very diverse electron-donating and electron-withdrawing sites. In this case the thermodynamic representation of complexation as a whole requires a determination not only of the difference in free energies but also that of the enthalpy (ΔH) and also entropy (ΔS), given by

$$\Delta G = \Delta H - T\Delta S.$$

Four possible combinations of ΔH and ΔS values, resulting in different bonding of the molecules in complexes, have been selected by Raevskii.[14]

1. There is a positive change in enthalpy and negative change of entropy on formation of a complex. In this case at all temperatures and absolute values of ΔH and ΔS the equilibrium will be displaced towards the initial compounds and complexation will not occur.

2. The change is enthalpy and entropy are positive. In this situation the final result of the reaction for complexation is determined by the ratio of the absolute values of ΔH and $T\Delta S$. There will be perceptible binding when $|T\Delta S| \gg |\Delta H|$.

3. The change in enthalpy and entropy are negative. In this case perceptible binding will occur when $|\Delta H| \gg |T\Delta S|$.

4. The change in enthalpy is negative and the change in entropy is positive. In this case for all ratios of the absolute values of ΔH and ΔS there is a maximum quantity of complex (in comparision with the first three examples).

These four possible combinations of the values of ΔH and ΔS do occur in molecular recognition processes. Highly specific recognition will occur when there are maximum absolute negative values of the difference between the enthalpy change of the recogniser interaction with the correct effector and that of its interaction with false effectors ($\Delta\Delta H$) and when there are maximum positive values of the difference in entropy change for these interactions ($\Delta\Delta S$).

It should be noted that in the vast number of publications on the thermodynamics of molecular recognition, the change in entropy is either neglected[15] or considered to be proportional to the enthalpy change, which is determined experimentally or from the change in calculated energy.[16] However, in a number of cases a significant contribution of the entropy factor to binding has been established. This relates in particular to the hydrophobic interaction which plays a significant role in biological systems. A clear example of the predominant contribution of entropy to the free energy is given by Hobza et al.[17] The significant influence of the relationship between ΔH and ΔS on the binding of ligands with receptors is convincingly shown in the study of Weiland et al.[18] It is clear from these results (Table 1) that the binding of agonists with an adrenergic receptor of turkey erythrocytes takes place with a large negative entropy, while antagonists display a relatively low enthalpy but an entropy that favours complexation. This in the complexation of *L*-adrenaline and practolol with this receptor with the same values of ΔG, binding occurs in the first case mainly because of a negative enthalpy while in the second case it occurs as a result of a positive entropy.

It is clear from these examples that a more fundamental understanding of the nature of molecular recognition is only possible when the entropy change is taken into account. Theoretical approaches to a calculation of entropy change are described in a review.[9] It is noted in this publication that for real biological systems the best method of determining the entropy change is to carry out calculations using molecular dynamics or the Monte Carlo method. However, considering the rather complex nature and high cost of such calculations, simple empirical approaches to a

determination of the changes in the thermodynamic properties of complexation should not be disregarded. Thus, a correlation between the difference in free energy and the number of covalent and ionic interactions has been reported,[19] and the difference in free energy has been calculated using a simple additive scheme.[20] In such approaches the noncovalent interactions have been divided into a number of components: hydrophobic, van der Waals, hydrogen bonding, dipole–dipole, ion–dipole, ionic, intensified ionic interactions, charge transfer, etc.[21] In order to assess the importance of the contributions of these components to the overall thermodynamic properties of specific interactions, a study of model systems in which one of the types of interaction is the predominant one is of particular importance. It is for this reason that in the present review a considerable amount of space is given to simple complexes with hydrogen bonding, complexes of macrocyclic ligands, and mixed complexes. It appears that a detailed study of such systems should favour a more precise simulation of substrate–receptor complexes.

Table 1. Thermodynamic properties of the binding of ligands with the β-adrenergic receptor of turkey erythrocytes at 310 K.

Ligands	ΔG, kcal mol^{-1}	ΔH, kcal mol^{-1}	ΔS, kcal mol^{-1} K^{-1}
Agonists:			
L-isoprenaline	−9.39	−13.39	−12.9
L-noradrenaline	−7.91	−18.86	−35.3
L-adrenaline	−7.50	−12.75	−16.9
Partial agonists:			
soterenol	−8.23	−7.84	+1.26
metaproterenol	−6.78	−10.83	−13.06
terbutaline	−6.19	−4.13	+6.65
Antagonists:			
L-propranolol	−12.51	−3.85	+27.9
pindolol	−11.85	−5.08	+21.8
zinterol	−9.13	−3.06	+19.6
metoprolol	−8.36	−0.66	+24.8
sotalol	−8.21	−2.15	+19.5
practolol	−7.46	+3.93	+36.7

III. Complexes with hydrogen bonding

1. Complexes with a single H-bond

The exceptional role of hydrogen bonding in the formation of specific substrate–receptor complexes has been quite well covered in the literature.[22–32] There is a large number of studies that contain information on an experimental determination of the thermodynamic properties of H-complexes. However, calculation methods are of greatest value for the simulation of molecular recognition, making possible an assessment of interactions in hypothetical complexes. Two approaches—quantum-chemical and empirical—can be selected here in relation to the calculation of the energy of an H-bond. At the present time quantum-chemical calculations are only applicable to small H-complexes[33–35] and this is a serious obstacle preventing their widespread application. For this reason in current methods of calculating H-complexes there is a predominance of empirical approaches—additive,[36–38] multiplicative,[39–42] and additive-multiplicative.[43,44] By using a multiplicative approach in the form of a "coefficient rule"[39] it was possible in two studies[45,46] to develop a single scale of hydrogen bonding, which led to the possibility of a quantitative comparison of electron-donating and electron-withdrawing capacities of different active sites.[47–49] The practical application of a single scale of electron-donating and electron-withdrawing coefficients in order to predict the enthalpy values of the hydrogen bonding of various molecules is only made possible by the development of a relatively simple system for calculating their values. In studies by Martynov and Raevskii[50–52] equations that relate the values of these factors with constants representing the electronic effect of the substituents form the basis of such a system. The algorithm of a programmed calculation of the values of electron-donating and electron-withdrawing factors has been reported.[53]

It should be emphasised that only the enthalpies of hydrogen bonding are discussed in the publications reviewed.[33–53] At the same time, as has already been stressed in the previous section, a knowledge of both the enthalpy and entropy change is needed for the thermodynamic treatment of complexation. At the present time, even though calculations of the change in entropy on formation of an H-bond have been carried out (see, for example, the study of Carsky and Urban[54]) they are complex and for that reason are not to be found very often in the literature. From this point of view there is interest in extending a simple multiplicative approach, as proposed[55] in a discussion of the experimental data on the complexation of electron-withdrawing phenols with various electron-donating compounds, to the problem of calculating the change in entropy.

The applicability of a multiplicative approach to the calculation of thermodynamic properties of hydrogen bonding of very diverse electron-donating and electron-withdrawing compounds has been specially tested.[56] In this study[56] data on the thermodynamic properties of 174 systems was analysed, 27 compounds acted as electron donors (dioxan, tetrahydrofuran, acetone, dimethylformamide, benzaldehyde, cyclohexanone, various sulphoxides, sulphodioxides, phosphoryl compounds, pyridine, acetonitrile, thiophosphoryl and selenophosphoryl derivatives), while 23 compounds acted as electron acceptors (substituted phenols, alcohols, carboxylic acids, and their halogen-substituted derivatives, amines, nitroamines, chloroform). By using this collection of data for determination of the values of electron-donating (E_j) and electron-withdrawing (E_i) factors, 174 nonlinear equations of the form:

$$\Delta H_{ij} = \Delta H_{11} E_i E_j,$$

were drawn up, where the values E_i of twenty-two acceptors (for phenol it is assumed that $E_i = -1.00$) and the values E_j of twenty-six donors (for diethyl ether $E_j = 1.00$) acted as unknown quantities. The solution of these equations led to a determination of the $E_i(E_j)$ values of all the compounds used in this study. It transpired that the electron-donating and electron-withdrawing capacity of the compounds varied over a wide range (E_i from −0.25 to −1.70 and E_j from 0.70 to 1.70) and were considerably dependent on the nature of the substituents at the active site. In this case the ranges of the $E_i(E_j)$ values for the different forms of active sites showed considerable overlap, which provides the opportunity for developing compounds that are capable of forming the required complexes from examples of different classes. A clear picture of the convergence of the experimental values of enthalpy and those calculated from $E_i(E_j)$ values is given by Fig. 1*a*. When

represented mathematically the correlation between ΔH_{calc} and ΔH_{exp} appears as the following:

$$\Delta H_{calc} = (-0.23 \pm 0.65) + (0.99 \pm 0.03)\Delta H_{exp},\ \text{kJ mol}^{-1}$$

$$(n = 174;\ R = 0.98;\ SD = 1.82;\ F = 5307)$$

Comparison of the data from particular systems showed that only in one out of 174 cases did the discrepancy between the experimental and calculated values of ΔH exceed 5.0 kJ mol^{-1}. In 18 systems the discrepancy was 3.0–4.5 kJ mol^{-1}. In the remaining 155 systems the calculated values were no different from the experimental values within the limits of experimental error. Thus the multiplicative principle for calculating the enthalpy of a hydrogen bond was borne out by studying a wide variety of electron-donating and electron-withdrawing compounds. It should also be emphasised that since the range of enthalpy change in the systems studied was 5.0–65.0 kJ mol^{-1}, the coefficient rule represents weak, medium, and strong H-complexes to the same extent.

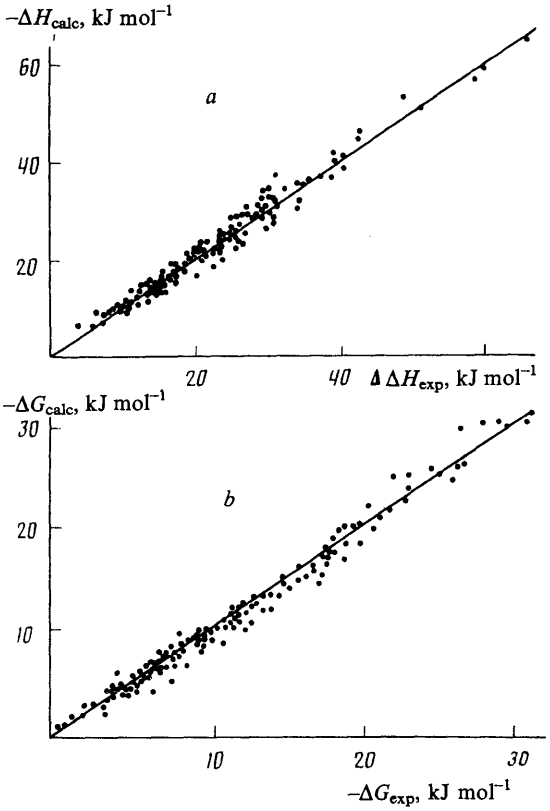


Figure 1. Graphical correlation of the experimental values and those calculated by an empirical multiplicative scheme for the enthalpy (*a*) and free energies (*b*) of H-complexes.[56]

In the same study[56] the coefficient rule was extended for the first time to free energy. For this the following equation was used:

$$\Delta G_{ij} = \Delta G_{11} C_i C_j,$$

where C_i and C_j are electron-withdrawing and electron-donating free-energy factors and ΔG_{11} is the free energy for complexation between phenol and diethyl ether in CCl_4 at 298 K. Formulation of 174 nonlinear equations of this type led to the derivation of the $C_i(C_j)$ values, which made it possible to calculate values of ΔG with an error no greater than the experimental error (Fig. 1*b*).

$$\Delta G_{calc} = (0.006 \pm 0.27) + (1.01 \pm 0.02)\Delta G_{exp}\ \text{kJ mol}^{-1}$$

$$(n = 174,\ R = 0.99,\ SD = 0.96,\ F = 8733).$$

Thus, by using the coefficient rule on the basis of the multiplicative principle it was possible to carry out accurate calculations of the thermodynamic parameters of hydrogen bonding. In order to demonstrate this, the experimental values of the difference in enthalpy and free energy and those calculated from the coefficient rule are given in Table 2 together with the binding constants for certain systems not included in the collection of data from which the values of the factors were calculated.

Table 2. Experimental and calculated values of the thermodynamic parameters of some H-complexes (solvent—CCl_4, 298 K, 1:1 complexes).[56]

Electron acceptor	Electron donor	ΔH, kJ mol^{-1}		ΔG, kJ mol^{-1}		log K, litres	
		exp.	calc.	exp.	calc.	exp.	calc.
C_6H_5OH	CH_3CN	14.2	12.5	4.50	4.16	0.79	0.73
n-ClC_6H_4OH	CH_3CN	15.1	13.5	4.73	5.12	0.83	0.90
CF_3CH_2OH	$HC(O)N(CH_3)_2$	25.5	23.2	9.18	10.04	1.61	1.76
CF_3CH_2OH	$CH_3C(O)N(CH_3)_2$	26.8	24.9	10.49	11.18	1.84	1.96
CCl_3COOH		33.0	34.1	14.08	10.8	2.47	1.89
		14.2	15.6	3.19	4.99	0.56	0.88

Apart from the collection of data used in this study[56] there is quite a considerable amount of information in the literature on the thermodynamic properties of hydrogen bonding of a wide variety of compounds. However, these data are incomplete and therefore for the time being cannot be used for a systematic analysis of electron-donating and electron-withdrawing functions of the active sites. Nevertheless, it may be assumed that the growing scientific interest in a quantitative measurement of intermolecular interaction and the improvement in measuring techniques and mathematical simulation will lead in the near future to a considerable expansion of experimental data that can be used to develop accurate calculation methods of the thermodynamic properties of hydrogen bonding.

It should be emphasised that the random collision of molecules is too "unreliable" a process for specificity to be exhibited.[57] It is necessary to define the direction of interaction. Hence a determination of the steric configuration of the interacting atoms in the molecular complexes is of considerable importance. The study of Murray-Rust and Glusker[58] is worthy of special mention here in relation to H-complexes. In this study, in order to determine the directivity of H-bonds involving sp^2- and sp^3-hybridised orbitals of

oxygen atoms, a systematic analysis of the structural data on several thousand of such compounds available on the Cambridge crystallographic data bank was carried out. Fairly strict requirements [effective localisation of the atoms, a small *R*-factor (less than 0.1), etc.] were applied to the selected data. In this case it was assumed that an intermolecular H-bond occurs when the distances between two electron-donating sites (one of which contains a hydrogen atom capable of forming a hydrogen bond) are less than 3.0 Å. Classification of the structural data on H-complexes of various cyclic ethers and ketones, epoxide compounds, acyclic ethers, ketones, esters, and other oxygen-containing compounds made it clear that hydrogen bonding occurs in all cases occurs preferentially in certain directions and that probably the most important factor is that zones of increased electron density from the unshared electron pairs (UEPs) are distributed along these directions. Thus, for ethers and epoxides hydrogen bonding occurs in a plane orthogonal to the plane of C–O–C, whereas for ketones and esters it occurs in the plane of CC(=O)Y, where Y = C, O. Murray-Rust and Glusker[58] concluded from this that the directivity of proton-donating groups towards UEPs is a characteristic feature of H-complexes.

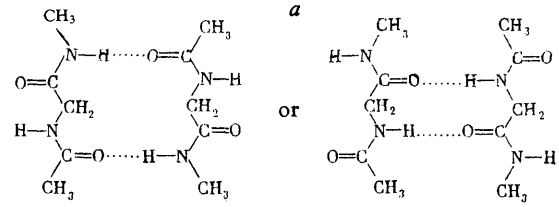
2. Complexes with several H-bonds

A study of the interaction of molecules, each of which contains several sites capable of forming H-bonds, is of particular importance in relation to molecular recognition. It is in these cases that there is a theoretical possibility for complexes with very large values of binding constants to occur both as a result of the summation of the enthalpies from each H-bond and as a result of the change in entropy in the conformational reorganisation of the interacting molecules providing the most convenient relative orientation of the atoms participating in the formation of H-bonds. Unfortunately, while there is quite an extensive amount of data on the thermodynamics, structure, and physicochemical properties of complexes with a single H-bond, the literature information on complexes with several H-bonds is very sparse. It is therefore useful to analyse the data from the few studies devoted to an experimental physicochemical investigation of such complexes.

A detailed study of the thermodynamics of the complexation of compounds, each containing two active sites, was carried out by Hopman.[59] In this study the thermodynamic parameters for autoassociation of 1-isobutyl-6-methyluracil (IBMU), γ-butyrolactam (BL), δ-valerolactam (VL), and ε-caprolactam (CL) were determined using UV-spectrophotometric titration, and their interaction with 2-aminopyridine (AP) and 2-aminopyrimidine (APM) was studied. Table 3 summarises the results obtained, which lead to the conclusions that: 1) while autoassociates of IBMU are least in strength, complexes of IBMU with AP and APM have a substantial value of the free energy difference because of the lower absolute value of the negative change in entropy in the series of compounds studied; 2) while the strength of complexes of BL with AP and APM are virtually the same, the free energy difference of the latter is twice as large as the former; 3) replacing the solvent (cyclohexane by benzene) has little effect on the enthalpy values of the reactions of both homo- and hetero-association (however, the free energy is markedly reduced). The results given above indicate with certainty that in the case of the hydrogen bonding of several sites a significant role is played by the steric structure of the interacting molecules. Unfortunately, the method selected in this study[59] can shed hardly any light in relation to this (as regards details about the effect of structure on complexation).

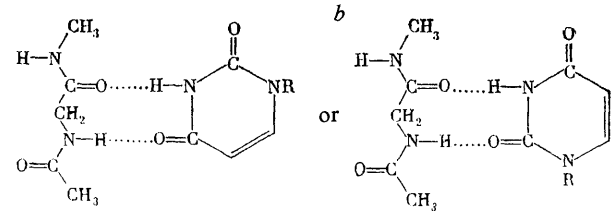
In one article[60] IR spectroscopy, which is more informative for determining structure, was used to study similar systems. In this case complexation between acetylglycine *N*-methylamide (AGMA) and 1-cyclohexyluracil (CHU) was studied. From the enthalpy value determined for homoassociation of AGMA and also the observed pattern of change in intensities of the bands with temperature and concentration, Carmona and Garcia-Ramos[60] were able to deduce that the homoassociates are dimers formed from each other:

a



The following structure was proposed for the heteroassociates:

b



It is noted here that since the ΔH values of heteroassociation do not constitute twice the value of ΔH for a single bond of this type, this suggests that steric hindrance has a considerable effect on complexation.

Table 3. Thermodynamic parameters for complexation of some compounds with two sites capable of forming hydrogen bonds (solvent — cyclohexane).[59]

System*	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	$-\Delta G$, kJ mol^{-1}
BL+BL	37.4	65.7	18.0
VL_VL	40.0	72.0	18.8
CL+CL	37.6	74.0	15.8
CL+CL	35.7**	101.0**	5.9**
IBMU+IBMU	18.3	24.7	11.0
BL+AP	25.2	68 8	4.9
BL+APM	25.8	55.0	9.8
VL+AP	23.0	58.6	5.7
VL+APM	23.3	54.6	7.2
CL+AP	25.3	62.9	6.7
CL+APM	25.5	48.9	11.0
CL+APM	24.3**	71.3**	3.3**
IBMU+AP	29.0	58.4	11.8
IBMU+APM	26.8	49.4	12.2

*For notation, see text; **solvent — benzene.

In another article[61] the possibility of forming simultaneously two H-bonds of the type NH...N and/or N–H...O is examined. 2-Aminopyridine and 2-pyridone were taken as research compounds.

In this study calculations on the energy of formation of H-complexes using the CNDO/2 method were carried out together with the collection of experimental data on the thermodynamic parameters of complexation. It was established that the enthalpy of dimerisation of 2-aminopyridine is approximately twice as high as the usual values of the enthlapy of complexation for compounds that each contain one nitrogen site and one-H-bond. Thus, formation of an eight-membered ring with four nitrogen atoms is very favourable in this case in terms of enthalpy. The enthalpy value for the formation of a 2-aminopyridine-2-pyridone complex was approximately half the sum of the energies of formation of 2-aminopyridine and 2-pyridone dimers. This is clearly a reflection of the multiplicative principle for electron-donating and electron-withdrawing functions as described in the previous section.

There are other publications in the literature related to a study of complexes with two H-bonds.[62–68] Unfortunately, there is no detailed information in these publications about the molecular structure of the complexes. This makes it very difficult to interpret the results and does not offer any idea about the nature and directivity of the H-bonds.

The progress in organic synthesis has had a considerable influence on studies relating to simulation of molecular recognition. As an example, reference may be made here to the studies of Rebek et al.[69,70] In these studies the problem was to synthesise a compound which would interact in a complementary manner with diamines and would thus serve as a model for the respective receptor. A model receptor containing two carbonyl groups and an acridine nitrogen atom was synthesised as this type of compound. A very polar environment of the hydrophobic skeleton of the molecules, which assists transport of this compound through biological membranes, should be regarded as a characteristic of its structure. The complex of this model receptor with purine has three H-bonds and very much resembles complementary biological systems. Thus, it is known that purine and pyrimidine derivatives, forming part of the polymeric molecule, DNA, act as monomer units in the storage of genetic information.

It is known that in the system of H-bonds that occur in DNA, the bases of one of the chains are joined to the bases of the other chain in a very specific manner, forming two H-bonds in a thymidine–adenine pair and three H-bonds in a cytosine–guanine pair. With regard to the problem of molecular recognition, particular attention should be given to studies relating to a determination of the stability of complexes of the different pairs of bases. The available literature data on the enthalpy of interaction of such bases[22,71,72] is given in Table 4. This material suggests that the guanine–cytosine complex which occurs in DNA is very much more stable than all of the others. As a reflection of this, using very simple calculations that took into account the strength of H-bonds, Pauling and Pauling[15] established that the probability of the wrong nucleotide entering a chain was approximately one in ten million.

It should be mentioned that at the present time there are many publications relating to a determination of the role of hydrogen bonding in substrate–receptor complexes. However, the use of this material for a discussion of the role of hydrogen bonding alone is complicated because of the occurrence of other types of interaction. Nevertheless, such studies provided a better understanding of the complex processes (the mechanism of the action of α-chymotrypsin,[73] proton transfer along hydrogen-bonded residues formed by hydroxyl groups in the side-chains of amino acids,[74–76] etc.).

It should also be noted that in the simulation of substrate–receptor complexes it is not possible to take into account hydration of the molecules that can affect both the interactive ability of the active sites and the conformational state of the partners. During the last ten years a great deal of attention has been given to this problem.[77–84] However, at the present time there is still much that remains unclear about the nature of the interaction of water molecules even with very simple organic compounds.

Table 4. ΔH values for homo- and hetero-association reactions of certain bases.[22,71,72]

Base pairs	$-\Delta H$, kJ mol^{-1}	
	gas phase	nonpolar medium
Adenine–uracil	58.0	24.8
Uracil–uracil	38.0	17.2
Adenine–thymine	52.0	—
Thymine–thymine	36.0	—
Guanine–cytosine	84.0	40.0–46.0
Cytosine–cytosine	64.0	25.2

IV. Synthetic macrocyclic biomimetics

The confirmation of the cyclic structure of valinomycin and the determination in the mid-1960's of the mechanism of this and other antibiotics led to the possible idea of synthesising macromolecules that are capable of selectivity binding metals that play an important part in biological processes and of transporting them through biological membranes. In 1967 Pedersen[85] reported the synthesis and complexing properties of such compounds. The first publications of Pedersen literally started an avalanche in the development of studies on the synthesis and use of these compounds both in fundamental chemical and biological studies and in a wide variety of applied fields.[86] Many thousands of the widest variety of ligands that can be classed as crown compounds have been synthesised to date. These are mainly coronands (containing classical crown ethers with oxygen, nitrogen, sulphur, and phosphorus atoms), cryptands (bicyclic polydentate ligands), podands (open-ring crown compounds), podand-coronands, oxocrowns, spherands, etc.[87] In the present section the complexing ability of such polydentate sytems towards a wide variety of ions and molecules will be discussed very briefly.

1. H-Complexes of macrocyclic compounds

18-Crown-6 is the most frequently used electron-donating compound for such complexes. In particular, its complexes with 4-nitroaniline,[88] 3-nitroaniline,[89] urea,[90] thiourea,[91] 4-nitro-1,2-benzdiamine,[92] and 2,4-dinitrophenylhydrazine[93] have been reported and studied.

Complexes of macrocycles involving the hydrogen atoms of methyl groups are of particular interest. Thus, Rogers and Green[94] reported the results of X-ray diffraction analysis of a complex between 18-crown-6 and nitromethane. This complex consists of a single crown ether molecule and two nitromethane molecules. In this case one nitromethane molecule is positioned above and the other molecule is positioned below the plane of the macrocycle, and each hydrogen atom of both methyl groups of the two nitromethane

molecules is connected by weak hydrogen bonds to one of the six oxygen atoms. The existence of H-bonds has also been established spectroscopically for this complex. A characteristic H-bond vibration has been detected in the far-infrared region.[95] Complex formation of this type has also been established for 18-crown-6 with the hydrogen atoms of the methyl groups of dimethylacetylene dicarboxylate,[96] bis(dimethyl) sulphone,[97] and dimethyl sulphate.[98] Complexes of other macrocyclic compounds with methyl and methylene groups have also been reported.[99,100] It appears that complexes of this type have still not been studied sufficiently. At the same time, the importance of noncovalent interactions of the type C–H...X in biological systems may be very considerable, since in substrate–receptor complexes there are many CH groups adjacent to electronegative substituents and having appreciable electron-withdrawing properties on account of this.

2. Complex formation with alkyloammonium cations

The interaction of macrocycles with ammonia and alkyl-ammonium compounds, in the same way as complexation between macrocycles and methyl groups, may be classed as "tetrahedral" recognition.[101] However, in this case, in addition to H-bonds, $N^+...O^{\delta-}$ electrostatic interactions also occur. The ratio between these two forms of interaction is 0.75:0.25.[102] In this case the strength and stability of the H-bonds depends to a considerable extent on the steric structure of the complexes. A group situated in the polar part of the molecule can affect the nature of complexation. The interaction of such groups with macrocyclic ligands can either destabilise the complex or increase its stability through hydrophobic and dipole–dipole interactions, H-bond formation, etc.

Complexes of the ammonium ion may be regarded as the simplest examples of this type of tetrahedral recognition. This ion forms complexes of medium stability with a large number of macrocyclic polyethers and cryptands. In the case of using a cryptand with four nitrogen atoms and six oxygen atoms as a ligand, an exceptionally stable complex is formed as a result of the considerable structural and energy complementarity.[103,104] As a result of such strong binding of NH_4^+ in a complex the pK_a value increases by six units. In the opinion of Lehn,[101] such effects of a change in pK_a values also exist in the active areas of enzyme molecules.

The effect of substituents in the amine group on the stability of complexes may be assessed from the results of Izatt et al.[105] It was shown that a substantial change in the nature of the substituents in NH_3Alk has little effect on the stability constants of its complexes with 18-crown-6. The effect of the structure of the macrocyclic ligand on the stability of complexes with a t-butylammonium cation has been studied in detail.[106] It was found that there was a considerable effect from the nature of the anion, the size of the ring, and the type of functional groups in the ring on the stability of the complexes. How strongly these structural features can affect the stability of such complexes is suggested by data on the discrimination of enantiomers of racemic salts by chiral macrocyclic ligands.

The concept of "chiral recognition" in the chemistry of macrocyclic compounds was developed by Cram et al.[107] using the analogy of the stereospecificity exhibited by high molecular residues in their interaction with low molecular substrates. In order for recognition of a chiral "guest" to be made possible, the "host" ligand must satisfy at least two conditions: 1) to have a cavity suitable for complexation; and 2) to have the conditions for energetically more stable interactions with only one of the two enantiomeric "guest" molecules to occur. A schematic representation of an example of "chiral" recognition is given in Fig. 2. The enantiomeric resolution achieved for the racemate of an ammonium salt[108] was obtained because in the (*R*) "host–guest" complex four strong noncovalent interactions in the cavity of the macrocycle occur whereas in the (*S*) "host–guest" complex there is no such steric correspondence.

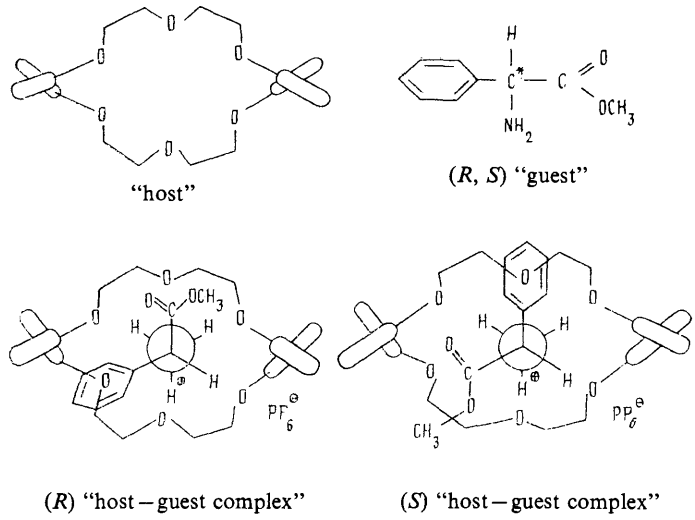
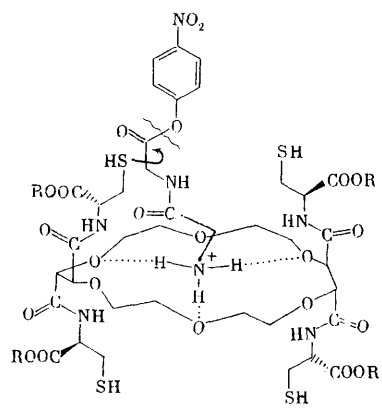


Figure 2. Schematic representation of an example of "chiral" recognition.[10]

In the simulation of enzyme systems, the process of cleavage of an ester bond, which occurs widely in metabolism, is often discussed. In the case of macrocyclic compounds it was possible to carry out this process using a tetra-*L*-cystinyl derivative which bound *p*-nitrophenyl esters of amino acids and peptides; *p*-nitrophenol was obtained as a result:[109]



In this case precise "chiral" recognition occurred between enantiomeric dipeptide esters. Many similar examples of the simulation of biological systems have been reported to date.[101,110,111] They have very considerable value for an understanding of the mechanisms of complex biochemical processes.

3. Complex formation with metal ions

The property of crown ethers that has been studied in the greatest detail is the "spherical" recognition of ions of alkali and alkaline earth metals. At the present time this topic is covered by a very large number of publications, which cannot be examined in detail within the scope of a short review. Therefore only the most prominent examples of a physicochemical study of such systems are given here. The X-ray studies of complexes of macrocycles with metal ions will be selected primarily (see several reviews[112–115]).

Let us consider 1:1 complexes between calcium and macrocycles as an example. The structure of a complex between calcium thiocyanate and 18-crown-6 has briefly been reported.[116] According to these findings, a coordination number of 8, which is typical for calcium, occurs for the metal in this complex, and the metal ion is situated inside the cavity of the macrocycle and lies at approximately the same distance from all six oxygen atoms of the macrocycle. The complex molecule has D_{3d} symmetry.

Quite a different situation has been identified in the complex of calcium nitrate with the same ligand.[117] In this case the complex molecule has C_2 symmetry. The calcium atom is also situated inside the cavity of the macrocycle. The nitrate groups act as bidentate ligands. The dihedral angles in two pairs of COCCOC residues have a *trans-gauche-trans*-conformation while in the third pair there is approximately a *trans-gauche-gauche*-conformation, with the dihedral angle in the CCOC fragment deviating by 37° from that which is usual for a *gauche*-conformation.

On the whole, the available data provide a basis for the conclusion that the conformational state of macrocyclic ligands in complexes is determined by the nature, not only of the cation, but also the anion.[118] This question has been studied in greater detail in the case of X-ray and spectroscopic analysis of benzo-15-crown-5 and its complexes with different calcium salts.[119] It was shown that the nature of the bonding between the electron-donating sites of the macrocycle and the calcium ion is determined by the combined interactions between the cation, anion, and macrocyclic ligand and electronically neutral molecules of water or solvent. This conclusion has been fully confirmed[120,121] with respect to the complexation of other macrocycles with calcium. Thus, in the established molecular structure of the complex between calcium and benzo-12-crown-4 that was isolated from acetonitrile solution, containing this ligand and calcium isocyanate as well as water of crystallisation,[120] the coordination sphere of calcium is formed by the four oxygen atoms of the macrocycle, the two nitrogen atoms of the isocyanate groups, an oxygen atom from one water molecule, and the nitrogen atom of a single acetonitrile molecule. In the case of the complex between calcium thiocyanate and dibenzo-24-crown-8,[121] the immediate environment of calcium is made up by four oxygen atoms of the macrocycle (two ether and two anisole), two nitrogen atoms of anionic isothiocyanate groups, and an oxygen atom of a coordinated water molecule. The four other oxygen atoms of the macrocycle do not participate in coordination. It appears that these types of calcium complexes of macrocycles can be regarded as models of bioorganic complexes.[122] It is possible to conclude from a number of publications[123–130] that there is evidence for competitive occupation of the coordination sphere during complexation of other metals with macrocyclic ligands. However, it should be noted in this case that a metal–ligand composition of not only 1:1 but also 1:2,[131] 2:1 [132,133] and 2:2 [134] is typical for such complexes.

Data on the thermodynamic properties of complexation of macrocyclic ligands with metal salts in solution are of considerable value in relation to molecular recognition. Considerable attention was given to this problem in the 1970's and 1980's. Several detailed reviews[135] and also the study of Buschmann‡ should be mentioned first of all. Of the original studies, mention may be made of the publication of Solov'ev at al.,[140] in which the thermodynamic properties of the complexes of two crown ethers (benzo-12-crown-4 and benzo-15-crown-5) with thiocyanate salts of lithium, sodium, potassium, calcium, and ammonia were obtained and analysed. It was established that in complexation between benzo-12-crown-4 and lithium and sodium, cation–ligand complexes occur with a composition of both 1:1 and 1:2. In the case of benzo-15-crown-5, 1:2 complexes are not formed for these salts. In complexation involving benzo-15-crown-5, the enthalpy of interaction with sodium, potassium, and calcium increases by 25% compared to benzo-12-crown-4, which may be regarded as evidence for the participation of an additional electron-donating site in complexation with benzo-15-crown-5. The entropy data are also very interesting. Thus, in complexes of lithium with benzo-12-crown-4 and benzo-15-crown-5 with composition 1:1, the enthalpy of interaction is virtually the same. At the same time, the value of the stability constant for the complex with benzo-15-crown-5 is higher by a factor of three. The small negative value of the entropy is thought to be the cause of this phenomenon. It is worth noting that in the case of the 1:2 complex between calcium and benzo-15-crown-5, the entropy change is even positive, resulting in a significant value of the stability constant even though there is a small enthalpy.

It is possible to assess how the structure of macrocyclic compounds affects their ability to bind metal ions from the data of Table 5.[141] It can be seen from Table 5 that the maximum binding results when there is a correspondence between the size of the cavity of the macrocycle and the diameter of the cation (complexation between potassium and 18-crown-6 and between caesium and

Table 5. Stability constants of 1:1 complexes of macrocyclic compounds with alkali metals in methanol at 298 K.[141]

	log K, litres mol^{-1}		
	Na^+	K^+	Cs^+
Tetramethyl-12-crown-4	1.41	—	—
Dicyclohexano-14-crown-4	2.18	1.30	—
Cyclohexano-15-crown-5	3.71	3.58	2.79
18-Crown-6	4.32	6.10	4.62
Cyclohexano-18-crown-6	4.09	5.89	4.30
Dicyclohexano-18-crown-6	4.08	6.01	4.61
Dibenzo-18-crown-6	4.36	5.00	3.55
21-Crown-7	—	4.41	5.02
Dibenzo-21-crown-7	2.40	4.30	4.20
24-Crown-8	—	3.48	4.15
Dibenzo-24-crown-8	—	3.49	3.78
Dibenzo-30-crown-20	2.00	4.60	—
Dibenzo-60-crown-20	—	3.90	—
Pentaglyme	1.52	3.20	—
Valinomycin*	0.67	4.90	—

*From the results of Lehn.[142]

‡ H J Buschmann *Stereochemistry of Organometallic and Inorganic Compounds* (Edited by I Bernal), Elsevier, Amsterdam–New York, 1987, p. 109.

21-crown-7). Data on an acyclic analogue — pentaglyme — and a natural ionophore — valinomycin[142] — are also given in Table 5. Comparison of these data shows that binding with macrocyclic ligands has a considerable advantage over binding with open ligands. The very high selectivity of the natural ionophore towards the potassium ion compared to the sodium ion attracts attention.

The discovery of the complexing ability of macrocyclic ligands towards alkali and alkaline earth metal was the basis for research into synthetic ionophores. Extensive studies, including a number cited here,[143–150] which led to both a better understanding of ion transport processes through biological membranes and the preparation of compounds of practical importance, have been carried out in this area up to the present time.

4. Complex formation with anions

In contrast to the coordination chemistry of cations and particularly metal ions, complexation involving anions has not been studied in sufficient detail. This situation is evidently at variance with the important role that is played by anions in chemistry and biology. That is obviously why interest in research in this area has increased markedly in recent years.[151,152]

Charged ammonium and electronically neutral residues containing strong electron-withdrawing atoms can act as atomic groups capable of binding anions. However, particularly stable and selective anionic complexes are obtained when macrocyclic molecules are used as receptors. In these cases the anionic substrate can enter the cavity of the receptor and can be stabilised in this position through different types of interactions. The structure of such complexes is analysed in detail in a study by Lehn et al.[153] A cryptand (BT) with six secondary and two tertiary amine nitrogen atoms and three ether oxygen atoms was used as the receptor. In the formation of a complex between this ligand and a fluoride ion, the latter occupies an asymmetrical position inside the cavity, probably because of the small size of the anion, and it coordinates tetrahedrally with four protonated nitrogen atoms (two from one chain and one each from two other chains). In the case of complexes with chlorine and bromine ions, the anions are positioned almost exactly on the axis joining the tertiary amine nitrogen atoms and are equidistant from them. In this case the anions are coordinated octahedrally with the six protonated secondary amine atoms through hydrogen bonds of the type NH...X. In the azide complex the N_3^- ion lies on the N...N axis, the two terminal atoms are at a distance of 3.24 and 3.21 Å from the tertiary amine nitrogen atoms of the ligand. In this case the terminal nitrogen atoms of the N_3^- ion form hydrogen bonds of virtually the same length (2.96 ± 0.04 Å) with the protonated secondary amine groups. These coordinate bonds form two tetrahedra. In both the free ligand and the three complexes studied an *endo,endo*-conformation occurs for the macrocyclic skeleton, with the tertiary nitrogen atoms turned towards the cavity.

Complex formation of this macrocyclic ligand with chloride, bromide, iodide, and azide anions, as well as with a number of organic and inorganic anions has been studied in solution by means of potentiometric titration (Table 6). It was established that stable complexes are formed with substrates that have the highest charge density such as the small-sized fluoride anion and polyphosphate ions. However, it follows from the literature data that when other polyammonium macrocycles are used as receptors, the binding of adenosine monophosphate (AMP^{2-}), adenosine diphosphate (ADP^{3-}), and adenosine triphosphate (ATP^{4-}) can be even more effective.[154]

The synthesis of the so-called co-receptors, which can bind either polyfunctional substrates or two or more small substrates at the same time[155] should be regarded as an important area of the chemistry of molecular receptors. Thus, polyammonium macrocycles that can effectively bind dicarboxylate anions have been obtained.[156] In this case there was a well-defined selectivity for formation of a complex between these macrocycles and dicarboxylates in whose molecules the coordination sites are separated by a different number of methylene bonds.

The significant change in ratio of the different free and bonded molecules when the solvent is varied for complexation of polyammonium macrocycles with anions is worthy of note. This evidently occurs as a result of the differing ability of partially and fully protonated structures to bind anions.

It should be mentioned in conclusion to this section that apart from the macrocyclic compounds described above, which are used as models of biological complexes related to the transport of substances and enzyme processes, synthetic porphyrins and nonporphyrinic tetraazomacrocyclic ligands have been widely used. The use of macrocyclic compounds as models of molecular recognition has also been described in reviews.[148,157–159]

Table 6. Stability constants of complexes of the two protonated forms of the macrocyclic BT ligand ($BT\text{-}6H^+$) and ($BT\text{-}5H^+$).[153]

Anion	log *K*, litres mol^{-1}		Anion	log *K*, litres mol^{-1}	
	BT-6H+	BT-5H+		BT-6H+	BT-5H+
F^-	4.10	3.20	$CH_2(CO_2)_2^{2-}$	3.10	2.00
Cl^-	3.00	1.95	SO_4^{2-}	4.90	2.90
Br^-	2.60	1.60	HPO_4^{2-}	5.50	2.75
I^-	2.15	1.55	AMP^{2-}	3.85	2.65
N_3^-	4.39	2.65	ADP^{3-}	5.85	4.15
NO_3^-	2.80	1.65	ATP^{4-}	8.00	5.40
HCO_2^-	2.30	1.50	$P_2O_7^{4-}$	10.30	6.45
$(CO_2)_2^{2-}$	4.95	3.35	—	—	—

V. Simulation of equilibria in aqueous solution

When the role of molecular recognition in specific biological processes is considered, the effect of the aqueous medium on the nature of complexation must also be taken into account. In a physiological medium a large number of chemical equilibria occur, in which hydrogen and metal ions and many biologically active compounds such as amino acids, peptides, proteins, carboxylic acids, organic phosphates, nucleic acids, and others participate. In this case there is competition between hydrogen and metals for the ligands. It should be emphasised here that even in a three-component system (one bivalent metal M^{2+} and two different bidentate ligands A and B) the formation of various species such as MA, MA_2, MB, MB_2, MAB is possible. In relation to molecular recognition there is particular interest in mixed complexes MAB. The probability of formation of the latter is twice as high compared to MA_2 and MB_2 complexes. Moreover, electrostatic and steric

interactions and hydrogen bonding,§ which is favourable for stable complexation, can occur in such mixed complexes.

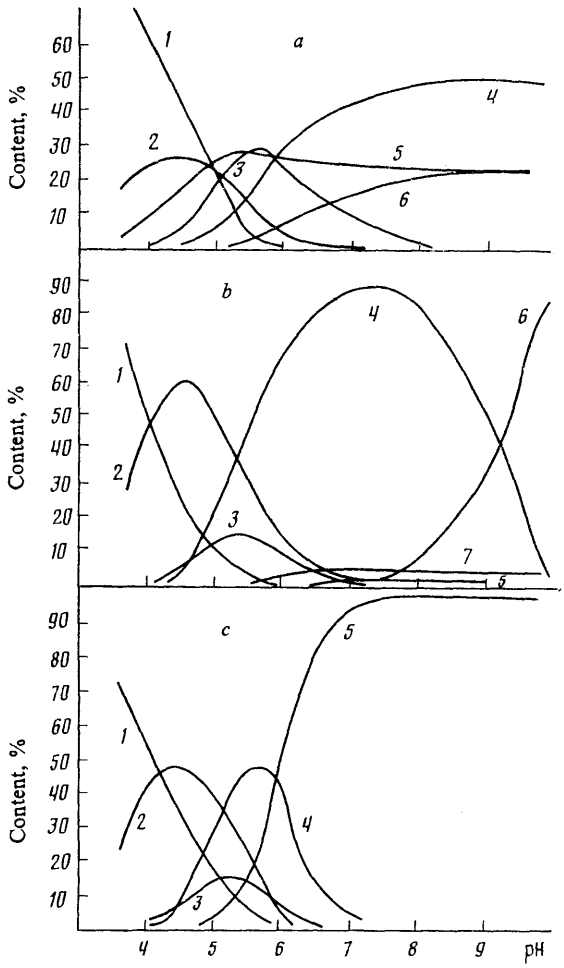


Figure 3. Graphical representation of the dependence of the composition of the following reaction systems: *a*, α-methylphenylaminophosphonic acid (MPAP) + *L*-phenylalanine (PA); the curves correspond to the change in Cu content (in %) in solution of: copper ion (curve *1*), Cu(PA) (curve *2*), Cu(MPAP) (curve *3*), Cu(PA)(MPAP) (curve *4*), $Cu(PA)_2$ (curve *5*), $Cu(MPAP)_2$ (curve *6*); *b*, MPAP + *L*-tyrosine (Tyr); the curves correspond to the change in Cu content (in %) in solution of: copper ion (curve *1*), Cu(TyrH) (curve *2*), Cu(MPAP) (curve *3*), Cu(TyrH)(MPAP) (curve *4*), $Cu(MPAP)_2$ (curve *5*), Cu(Tyr)(MPAP) (curve *6*), $Cu(Tyr)_2$ (curve *7*); *c*, MPAP + *L*-dihydroxyphenylalanine (Dopa); the curves correspond to the change in Cu content (in %) in solution of: copper ion (curve *1*), Cu(Dopa-H) (curve *2*), Cu(MPAP) (curve *3*), Cu(Dopa)(MPAP) (curve *4*), Cu(Dopa)(MPAP) (curve *5*); the content of $Cu(MPAP)_2$ and $Cu(Dopa)_2$ was less than 3%.

§ V V Lukachina *Ligand–ligandnoe Vzaimodeistvie i Ustoichivost' Raznoligandnykh Kompleksov* (Ligand–ligand Interaction and the Stability of Heteroligand Complexes), Naukova Dumka, Kiev, 1988, p. 181.

Another important characteristic of complexation in an aqueous medium is the change in the number of different complex species when the medium is varied. This results from the possible interaction of ligands with hydrogen ions when there is a change in their electron-donating properties. Since the pH values of the medium differ considerably in different parts of the organism, a study of such systems is particularly important for an understanding of molecular recognition under natural conditions.

The structure and stability of mixed complexes have been discussed in detail in three reviews.[160–162] Data on the composition of complex species in systems containing copper and two amino acids are displayed in the form of graphs in Fig. 3. A study is made on four types of system, in which one of the amino acids, namely, α-methylphenylaminophosphonic acid (MPAP), is present in all four cases, while the second varies, leading to substantial changes in the stability of the resulting complexes.[163] In the system MPAP–PA–Cu (Fig. 3*a*) a mixed complex is formed in quantities not exceeding its statistical proportion, while in the system MPAP–Dopa–Cu (Fig. 3*c*) it is evidently in excess of all other complexes. There has been a growing emphasis on studying such systems in recent years aimed at a better understanding of the complexation processes in a physiological medium and the potential practical application of the selective nature of bonding.[164–172]

To what extent competitive complexation can affect the composition and distribution of complex species in a physiological medium can be assessed from the results of calculation of a model plasma in the absence of EDPA and when this ligand is added.[160] It follows from the results in Table 7 that the addition of EDTA leads to its complete binding of zinc and copper, has a considerable effect on the type of calcium complexes, and in actual fact has no effect on the distribution of magnesium. The calculations carried out clearly demonstate that because of such a complex action on the plasma,

Table 7. Distribution of complexes in a plasma model.[160]

Type of species		Content, %		Type of species		Content, %	
metal	ligand	without EDTA	with EDTA	metal	ligand	without EDTA	with EDTA
Ca	Globulin	24.0	15.0	Zn	Histidine, cysteine	3.4	—
Ca	Albumin	16.0	13.0				
Ca	Bicarbonate	7.6	4.3	Zn	Cysteine, histidine	2.1	—
Ca	Citrate	2.4	2.0				
Ca	Phosphate	0.8	0.5	Zn (free)		4.7	0.0
Ca (free)		49.0	28.0	Zn	EDTA	—	99.99
Ca	EDTA	—	38.0	Mg	Bicarbonate	12.0	12.0
Zn	Cysteine, histidine	19.0	0.0	Mg	Phosphate	4.3	4.2
				Mg	Citrate	2.4	3.0
Zn	$(Cysteine)_2$	16.0	0.0	Mg	Lactate	0.6	0.6
Zn	$(Histidine)_2$	13.0	0.0	Mg (free)		80.0	78.0
Zn	Albumin	13.0	0.0	Mg	EDTA	—	1.5
Zn	Glycine, histidine	6.2	—	Cu	Histidine, cysteine	44.0	0.7
Zn	Histidine	3.6	—	Cu	Histidine, cysteine	38.0	0.6
Zn	Citrate	3.6	—				
				Cu	$(Histidine)_2$	16.0	0.3
				Cu	EDTA	—	98.3
				Other species		0.3	

Note. Metals and EDTA were at the following concentrations (in moles): $[Ca] = 2.5 \times 10^{-3}$, $[Mg] = 1.1 \times 10^{-3}$, $[Zn] = 46 \times 10^{-6}$, $[Cu] = 1.1 \times 10^{-6}$, $[EDTA] = 1.0 \times 10^{-3}$.

the use of EDTA as a pharmacological compound that assists the binding of free calcium can have very unfavourable results. It seems that such calculations should become an essential element of studies that precede the pharmacological insertion of ligands which effectively bind biometals.

In examining complex equilibrium systems in solution, we should not omit the progress made in programming[179] using the Newton method,[174] Simplex method,[175] Monte Carlo method,[176] and others.

VI. Computer-aided molecular simulation

The general principles of this method have been presented in sufficient detail in several studies.[177-184] Within the scope of this review it should be noted that the most important feature of any molecular computer model is its energy. In principle, quantum mechanics can provide a basis for the calculation of the molecular energies of biologically active compounds.[8-10,184,185] However, the complexity of the research subjects makes it necessary in practice to use various approximations with the calculation of force field parameters based on experimental data. Vibrational spectra are used to determine the force constants. Information on the bond lengths and bond angles obtained from X-ray diffraction analysis, gas electron diffraction, neutron diffraction, and microwave spectroscopy is used for a determination of the geometric parameters. The parameters of the interactions between nonbonded atoms are often determined from thermodynamic data (heats of mixing, evaporation, etc.).

In the computer-aided molecular simulation of a specific compound using systems that comprise a minicomputer, computer graphics, and also a data bank of structural and physicochemical properties, the design of the initial structure is carried out at the first stage. Then calculations are carried out, leading to an optimisation of the molecular geometry and a determination of the possible electronic and steric structure of the molecule and its energy properties. In this case, since the molecules of biologically active compounds usually contain several axes of internal rotation and hence have many stable conformations that are similar in energy, special routines of systematic scanning of such conformations are used.

A significant contribution to a more fundamental understanding of the structure of molecules under real conditions is provided by the computer-aided simulation of the dynamic properties of chemical systems based on the Monte Carlo method[8,186,187] and that of molecular dynamics,[188-191] which make it possible, in principle, to calculate also the entropy.[192,193]

Computer-aided simulation of molecular recognition can be carried out using calculations on the competitive interaction of several ligands (L_I, $L_{II} \ldots L_N$) with a receptor (R). If the entropy contribution to this process is neglected, by analogy with the study of Fruhbeis et al.[184] we can write:

$$\Delta E(L_I) = E(RL_I) - E(R) - E(L_I),$$
$$\Delta E(L_{II}) = E(RL_{II}) - E(R) - E(L_{II}),$$
$$\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\Delta E(L_N) = E(RL_N) - E(R) - E(L_N).$$

A negative ΔE value is necessary for the formation of a complex, and for highly selective binding of L_I with the receptor, the following condition must be fulfilled:

$$|\Delta E(L_I)| \gg |\Delta E(L_{II})|, \ \ldots \ |\Delta E(L_N)|.$$

Thus, in order to assess the recognition between molecules L and R, it is necessary to have information on the steric structure and energetics not only of the molecules themselves but also for the corresponding complexes. According to Humphries,[194] three aspects need to be considered in the scanning of stable conformations of a complex: the relative orientation of L to R, the optimum conformations of L in contact with R, and the optimum conformations of R in contact with L. All these questions have now been successfully resolved using computer docking of molecules.[182,184,195,196] This is assisted by quite a well developed contemporary mathematical facility for molecular computer graphics, which makes it possible to carry out numerous manipulations on the display screen: to represent the molecules as a combination of bonds (Dreiding models) or as overlapping spheres of atoms. The image can be rotated, fragmented, superimposed, put in perspective, etc.[197,198]

It is very important to emphasise that the methodological developments in computer-aided molecular design as described above have been applied very quickly to the development of biologically active compounds. There are a number of review articles on this topic.[2,19,199-202] As an example we can examine a recent publication,[203] in which the computer analysis of basic structures for interaction with papain and carbonic anhydrase was carried out. The X-ray diffraction data on these enzymes were taken from the study of Bernstein et al.[204] Compounds selected from the widely used Cambridge databank of X-ray diffraction data were investigated as interaction partners. Docking of the active sites of the pairs of molecules was carried out using a programmed procedure described by Kuntz et al.[205] Amongst the identified compounds whose active sites were effectively docked with papain were: 3-iodophenyl hippurate (IPH) (a known substrate of this enzyme), a derivative of trimethoxybenzamide (TMB), and three macrocyclic compounds—2,6-pyridine-24-crown-8 (PC8), 10,10-ethylene-bis(1,4,7-trioxa-10-azocyclododecane) (TACD), and 2,2-bis(4,4-benzophenono(2,6)naphthalenophane) (BPN). The calculated energies of these ligands and their complexes with papain are given in Table 8. The results in Table 8 are an indication of the high stability of these complexes.

Table 8. Energies of complexation of a number of compounds with papain (calculated value of the free energy of papain is equal to 266.2 kJ mol^{-1}).[203]

Ligand	E_L, kJ mol^{-1}	E_C, kJ mol^{-1}	E_I, kJ mol^{-1}
PC8	22.5	−2784.0	−141.3
TACD	60.2	−2712.7	−117.7
TBA	145.6	−2555.1	−135.6
BPN	82.2	−2696.0	−113.0
IPH	24.7	−2741.2	−100.7

Note. For ligand notation, see text; E_L—energy of free ligand; E_C—energy of complex; E_I—energy of interaction.

In recent years studies of computer-aided methods for the simulation of molecular recognition have been increasingly extended to a determination of the relationships between the structure of

compounds and the biological activity which they exhibit. In particular, simulation has been carried out for the inhibition of dihydrofolate reductase,[206,207] and elastase,[208] the binding of DNA,[209] adrenergic and muscarinic receptor systems,[210,211] the complexation of ligands with a serotonin receptor[212] and cytochrome,[213] the mimetics of α-chymotrypsin,[214] the inhibition of photosynthesis,[215] the reactions of ribonucleic acid with synthetase[216] and different drugs with tubulin.[217]

The simulation of bioorganic complexes in an aqueous medium may be regarded as a close approximation to reality. Thus, the results of studies on the effect of hydration on ionic permeability processes have been correlated.[218] In these studies complexes of valinomycin, nonactin, and dialkyl-substituted dibenzo-18-crown-6 with potassium[219–221] and antibiotic X 537 A with serotonin, dopamine, noradrenaline, and adrenaline[222] have been investigated. The ionic channels formed in a lipid membrane by gramicidin A [223] and amphotrycin B [224] have also been simulated.

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In view of the progress made in the 1980's in the fine organic synthesis of model compounds, physicochemical techniques, mathematical methods for analysis of the properties of complex equilibrium systems, and computer-aided molecular design it is possible to agree with the view that "we are starting to recognise the molecular parameters which control the reactions of ligands with macromolecules".[2] However, in order that the concept of molecular recognition should become a firm principle in the directed search for compounds with given properties, further development of fundamental studies in many areas is necessary. This primarily concerns studies to determine the thermodynamic properties of H-complexes in different solvents in order to identify the principles concerning the effect of the medium on complexation. The extremely sparse amount of information at present on the detailed molecular structure and thermodynamics of complexes with several H-bonds should also be mentioned.

Determination of the role of the entropy factor in the binding of substrate–receptor complexes is of particular importance for a more fundamental understanding of molecular recognition. At the present time the entropy effect is neglected in the vast majority of studies. However, there are findings which suggest that a decisive role is actually played by this factor, for example, in the complexation of different ligands with similar enthalpy values. Hence, the usefulness of experimental studies to determine the entropy as well as calculations, particularly those using the Monte Carlo method and molecular dynamics, is evident.

In the final section of this review the growing contribution of computer-aided molecular simulation to the study of molecular recognition was noted. For all the evident merits of this method, it should not be forgotten that it is based on fairly incomplete knowledge of the nature of intra- and inter-molecular interactions. On this basis it seems reasonable to combine the different types of studies so that the models of molecular recognition can be constantly improved through the application of accurate new experiments as well as theoretical developments.

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Reactions involving the heterolytic cleavage of carbon–element σ-bonds by Grignard reagents

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ABSTRACT. The reactions involving the heterolysis of the C–O, C–C, C–N, C–S, C–Cl, etc. bonds by organomagnesium compounds are examined and the nature of this interesting phenomenon is analysed. On the basis of the analysis of the characteristic features of the cleavage under discussion, it is shown that the heterolysis of the carbon–element bond is, firstly, a general reaction for all classes of organic compounds (provided that two conditions are observed: the substrate molecule must fragment into two stable species—a carbonium ion and an anion—and the strength of the Lewis acid properties should be adequate for the occurrence of the above reaction) and, secondly, the heterolysis of the carbon–element bond is one of the independent pathways in the reactions of the Grignard reagents.

The bibliography includes 158 references.

Contents

I. Introduction 234
II. The structure and reactivity of Grignard reagents 234
III. Reactions involving the heterolysis of carbon–element σ-bonds by Grignard reagents 237
IV. Conclusion 247

I. Introduction

For more than 85 years investigators have been studying extensively Grignard reagents in organic synthesis, especially in nucleophilic addition and substitution reactions. This is apparently why, for historical reasons, chemists concentrated attention on the nucleophilic properties of organomagnesium compounds and regarded these reagents as typical nucleophiles. The Lewis acid properties of Grignard reagents were hardly taken into account in assessing their reactivity. Nevertheless, the initial coordination of the RMgX (R_2Mg, MgX_2, $R_2Mg.MgX_2$) molecules via the free electron pair of the most nucleophilic heteroatom of the substrate has been frequently included in the mechanisms of the reactions of Grignard reagents with various compounds.

It has been shown that, on the one hand, this intensifies the deficiency of the electron density on the reactive carbon (element) atom, which is as a rule linked to the heteroatom via a σ- and π-bond. On the other hand, the coordination considered increases the nucleophilicity of the reagent cryptobase.

Thus the coordination (i.e. Lewis acid) properties of the reagent merely assist in a more striking manifestation of the nucleophilic properties. The reactions proceeding via this mechanism (and this happens in most cases) have been referred to as "normal". Those which do not fit into the framework of the above mechanism have been called the "anomalous" (including reduction and enolisation reactions).

The segregation of processes in which the Lewis acid properties of RMgX merely supplement the nucleophilic properties greatly simplifies the understanding of the nature of this reagent but does not therefore provide a complete and correct idea about its reactivity.

The dual nature of the Grignard reagent consists in the fact that, in reactions with molecules whose skeleton is extremely sensitive to the action of weak Lewis acids, the initial coordination of RMgX (R_2Mg, $MgX_2.R_2Mg$, etc.) already leads to pronounced and irreversible changes in the molecular skeleton and to the appearance of new reaction centres not provided for by the mechanism of the "normal" nucleophilic addition. In such cases, the Lewis acid properties of organomagnesium compounds determine the structure and yield of the reaction products. The application of the term "anomalous" to these reactions is illegitimate.

This review deals with reactions in which the structure of the products is determined precisely by the Lewis acid properties of RMgX.

II. The structure and reactivity of Grignard reagents

1. The structure of RMgX

In a review published in 1980, Ashby[1] traced the development of ideas about the structure of organomagnesium compounds in solutions in organic solvents. He proposed a model described by the following scheme:

$$\ldots \rightleftarrows \text{trimer} \rightleftarrows \text{dimer} \rightleftarrows 2RMgX \rightleftarrows R_2Mg + MgX_2 \rightleftarrows \text{dimer} \rightleftarrows \text{trimer} \rightleftarrows \ldots \quad (1)$$

The above scheme takes into account the possibility of the establishment in solution of the Schlenk equilibrium and the formation of dimers, trimers, and more complex associated species. In view of their insignificant amount, ionic species have not been included in this scheme.

The Schlenk equilibrium for isobutylmagnesium bromide[2] and t-butylmagnesium bromide[3] in solution in tetrahydrofuran (THF) was investigated by ^1H NMR spectroscopy and that of dicyclopentadienylmagnesium was studied by ^{25}Mg NMR spectroscopy.[4] It was shown that the equilibrium depends greatly on the reagent concentration and to a lesser extent on temperature.

In a later study[5] the existence of the Schlenk equilibrium in solution was questioned. According to the authors,[5] the following equilibria occur in solution in THF:

$$4[RMgX(THF)_n] \rightleftarrows 2[MgR_2(THF)_2] + [MgCl_4]^{-2} + [Mg(THF)_6]^{+2}, \quad (2)$$

$$4[RMgX(THF)_n] \rightleftarrows [(THF)_nMg(\mu\text{-}Cl)_2MgR_2] + [RMg(\mu\text{-}Cl)_2MgR(THF)_3]. \quad (3)$$

The above scheme, extended also to other solvents and other halogen atoms, was proposed on the basis of indirect data. Thus $[NBu_4]_2MgCl_4$ and $[(THF)_4Mg(\mu\text{-}Cl)_2FeCl_2]$ have been isolated from a solution of a Grignard reagent. According to Sobota and Duda,[5] $MgCl_2$ is too reactive to exist in solution in a free state. On this basis, the existence of the Schlenk equilibrium is in fact rejected.

The evidence presented by Sobota and Duda[5] is apparently inadequate and too controversial to question the existence of the Schlenk equilibrium, but it is necessary to take into account Eqns. (2) and (3) in considering the structure of RMgX in solution.

In the study of equilibria involved in Scheme (1), it has been noted[6,7] that the equilibrium depends on many factors — the nature of the organic group, the halogen, the temperature, the concentration of the organomagnesium compound investigated, and the solvent. The influence of the solvent, or more precisely of its solvating capacity, on the equilibrium plays a decisive role under these conditions.

The solvating capacity of the solvent is a complex function of the coordination properties of the heteroatom involving the lone electron pairs of the solvent and the steric hindrance of the coordination of its molecules to the substrates.[8] For this reason, the solvating capacities of solvents can be compared only when their basic properties are referred to the Lewis acid properties of a specific substrate.

The quantity serving as a measure of the solvating capacity of the solvent relative to a given Lewis acid can be estimated from ^1H NMR spectra.[9,10] The strength of strong Lewis acids relative to a given base can be estimated similarly.[11]

Another approach to the quantitative allowance for the effect of steric and basic properties of the solvent on its solvating capacity has been proposed by Tuulmets and co-workers.[12–14] They introduced the function B^* — the effective basicity characterising the solvating capacity of the solvent relative to a given Lewis acid (organomagnesium compound):

$$B^* = B(B_0/B + \varphi^* + E_s^{0'}).$$

The quantities B and $E_s^{0'}$ — characteristics of the basic and steric properties of solvent molecules — have been tabulated. The values of the effective acidity index φ^* of the reference substrate can be calculated from the following correlation equation:

$$\varphi^* = 10.1 + 2.4\,E_s^{0'} + 0.6\,\Sigma\sigma^*. \quad (4)$$

where $E_s^{0'}$ are the isosteric constants of the substrate molecules and $\Sigma\sigma^*$ is the sum of the inductive constants of the cryptobase and the halogen of RMgX. These have been tabulated. B_0 is a constant.

Thus the quantity B^* characterises the effectiveness of the interaction of the selected reference substrate with the solvent, the decisive role being attributed, according to the author,[12] to steric hindrance of coordination.

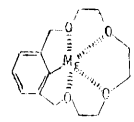
It follows from Eqn. (4) that the quantity φ^* serves as an estimate of the effectiveness of the interaction of the Lewis acid with the molecules of the given solvent and the effective acidity indices were therefore used by the author[12] to determine the position of the Schlenk equilibrium:

$$K_{Schl} = -\gamma(2\varphi^*_{RMgX} - \varphi^*_{R_2Mg} - \varphi^*_{MgX_2}), \quad (5)$$

where γ is a characteristic of the base, entering as a proportionality coefficient between the left- and right-hand sides of Eqn. (5).

The structural transitions defined by Eqn. (1) and occurring in solvents can be understood more readily by determining the driving force of the processes described — the coordinative unsaturation of the RMgX molecule. This is manifested primarily by the formation of complexes by organomagnesium compounds (Table 1).

Table 1. Composition of the complexes formed by RMgX.

Ligand (L)	Composition of the complex RMgX : L	Refs.
Ph^-	$[Li(TMEDA)^*]_2Mg_2Ph_6$	[15]
Ph^-	$LiMgPh_3$	[16]
Ph^-, H^-	$KMgPh_2H$	[17]
$(CH_3)_2N(CH_2)_2NHCH_3$	$(CH_3)_2Mg \cdot L$	[18]
$N[CH(CH_3)CH(CH_3)OCH{-}CH{-}OCH_3]_3$ (CH$_3$ CH$_3$)	$CH_3MgI \cdot L$	[19]
$(CH_3)_2N{-}(CH_2)_2O(CH_2)_2OCH_3$	$PhMgBr \cdot L$	[20]
$[(CH_2)_3{-}O{-}(CH_2)_3]^{2-}$		[21]
		[22]

* TMED = tetramethylethylenediamine.

The magnesium in Grignard reagents can have different coordination numbers in crystals and in solution but in a solvent a coordination number of four is most characteristic of these compounds.[23]

In the absence of the solvent (either at high concentrations or in the case of weak interactions with the solvent molecules), the hypothetical RMgX molecule is then coordinatively unsaturated. The coordination saturation of asymmetric organomagnesium compounds is attained in this instance as a result of the creation of halogen bridges[24] or alkyl(aryl) bridges.[25] Symmetrical organomagnesium compounds form polymer chains in the solid state[26] while in solution they give rise to self-association species formed via alkyl(aryl) groups.[2,27]

The solvent molecules competing with the halogen atoms and the atoms of the organic group for coordination sites at the magnesium atom hinder the formation of self-associated species, and the greater the solvating capacity of the solvent the more intense is this competition. This is why highly basic solvents not only decompose

the conglomerates RMgX (X = Br, I) at low reagent concentrations as far as monomeric species but they also solvate effectively the symmetrical molecules of organometallic compounds, displacing the Schlenk equilibrium to the right. This claim is confirmed by the weaker effect of solvation on the rate of exchange of organic groups in symmetrical Grignard reagents compared with the asymmetric reagents.[9]

Certain halogen bridges (X = F, Cl) are so strong that a highly solvating solvent cannot disrupt them and the molecules of the organomagnesium are associated even at high dilution.[1] On the other hand, in the presence of a highly electron-accepting substituent in the skeleton of the cryptobase, for example, fluorine atoms (R = C_6F_5), certain Grignard reagents behave even in weakly basic solvents as if they were placed in highly basic solvents. This is reflected not only by the absence of association but also by a rightward shift of the Schlenk equilibrium.[28]

Since the substrates used in reactions with Grignard reagents have lone electron pairs in the heteroatoms, they are all Lewis bases. When these substrates are introduced into a RMgX solution, they begin to compete with solvent molecules for coordination sites at the magnesium atom. The ability of Lewis bases to complete with solvent molecules and the strength of the Lewis acid properties of RMgX determine in many respects the reactivity of the organomagnesium compound.

2. The reactivity of RMgX

The reactions of organomagnesium compounds with various substrates are difficult to study because even in the simplest case (at high dilution and for X = Cl, Br, or I) there exist in solution at least three, in conformity with the Schlenk equilibrium, species with different reactivities.

It has been found that in many instances symmetrical organomagnesium compounds are more reactive than asymmetric compounds,[29,30] while the opposite behaviour was noted in other cases.[31]

The reactivities of monomeric and polymeric forms are in its turn also different, as shown by a number of workers.[32,33]

When the amount of Grignard reagent is equivalent or deficient, the primary products of the addition reagent—magnesium enolates or alkoxides—can themselves function as competing reactants.[34,35] The competitive reactions are suppressed by a large excess of the Grignard reagent.

Thus the reactivity of organomagnesium compounds is equal to the sum of the reactivities of all the magnesium-containing species present in solution.

(a) Nucleophilic, basic, and reducing properties of RMgX. It has been suggested[36] that the entire wide variety of reactions of organomagnesium compounds proceeding via the polar mechanism be divided arbitrarily into two main types in terms of the effect of solvation on their course, for example:

$$R_2C{=}O + R'MgX \rightarrow R_2R'C{-}OH \text{ addition—first type;}$$

$$RMgX + R'X \rightarrow R{-}R' + MgX_2 \text{ substitution—second type.}$$

The reactions of the first type are inhibited and those of the second type are promoted with increase in the solvating capacity of the solvent.[37] Intense solvation polarises the Mg—C bond, enhancing the electron-donating properties of the α-carbon atom of the cryptobase of the organomagnesium compound, on the one hand, and blocks the coordination sites at the magnesium atom, on the other.[37]

In the reactions of the first type, the nucleophilic attack on the cryptobase R^- is preceded by the coordination of the Grignard reagent to the carbonyl compound with formation of a complex. The existence of such complexes has been confirmed spectroscopically.[38,39] It is believed that this stage enhances the electrophilic properties of the attacked carbon atom.[40]

Weakly basic substrates, for exzmple $C_2F_5CH{=}O$, cannot displace solvent molecules and give rise to reactions of an intermediate type occurring without preliminary coordination.[41]

In reactions of the second type, the coordination of RMgX to the substrate does not play a decisive role and Grignard reagents behave like typical nucleophiles.[42]

We believe that there exists a further type of reactions of organomagnesium compounds proceeding via a polar mechanism. The substrate cleavage (isomerisation) reactions under the influence of RMgX belong to this type. These reactions proceed as a rule in weakly basic solvents, highly basic solvent retarding or fully inhibiting them. Not only the primary coordination of RMgX but also the Lewis acid strength of the reagent are important for reactions of the third type.

In our view, highly solvating solvents weaken the acid properties of organomagnesium compounds. This fact is important because, whilst causing an overall retardation of addition reactions, intense solvation makes their occurrence possible. Under the conditions of intense solvation, cleavage (isomerisation) reactions are as a rule inhibited.

Since reactions of the third type take place via a carbonium-like state (or via the intermediate formation of a carbonium ion, the solvation (stabilisation) of these states plays an important role in the above reactions. Therefore, if the solvating capacities of the solvents do not differ greatly, cleavage (isomerisation) reactions can take place in solvents with a higher solvating capacity as a result of the solvation stabilisation of carbonium-like transition states.

In order to understand the structures and yields of the products of the reactions of RMgX with various substrates, we shall now turn to conclusions reached for reactions of ketones with RMgX.[42–44] In the first place, in the presence of a large excess of RMgX magnesium alkoxides and enolates compete weakly with the Grignard reagent in addition, enolisation, and reduction reactions. Consequently, ketones react with RMgX via three main pathways.

The influence of structural differences in these three reactions is susceptible to quantitative interpretation. The partial rate constants for the reactions of ketones having the general formula $RCOCH_3$ with RMgX can be calculated from the following equations:

$$\lg(K_{add}/K_0) = \rho^*\sigma^* + \delta E_s^0 + h\Delta n, \quad \text{(Ref.42)}$$

$$\lg(K_{red}/K_0) = \rho^*\sigma^* + \delta E_s^0, \quad \text{(Ref.43)}$$

$$\lg(K_{enol}/K_0) = \delta\Sigma E_s^0. \quad \text{(Ref.44)}$$

The influence of the inductive effect of the group R on the addition constant (K_{add}) and the reductive constant (K_{red}) is taken into account by the first term in the equations (σ^* are the Taft inductive constants of the substituents). The steric hindrance in the addition and reduction reactions is described by the term δE_s^0 (the steric constant of the substrate group R) and enolisation (the enolisation constant K_{enol}) is described by the term $\delta\Sigma E^0$ (the steric constants of the substituents at the α-carbon atom of the ketone).

The third term ($h\Delta n$) in the equation describing the kinetics of the addition reaction takes into account the influence of the C–H and C–C σ-bonds in the α-positions. Among the wide variety of factors influencing the rates of parallel reactions, steric factors are believed to play a decisive role.[42–44]

The study of the kinetics of the reactions of ketones with RMgX enabled the authors[42–44] to conclude that, for the three reactions analysed, the transition state has a structure close to that of the initial compounds, i.e. the ketone and RMgX, and in this sense they can be regarded as related. One cannot therefore differentiate one of them (addition) as the only "correct" or "normal" reaction of RMgX with carbonyl compounds.

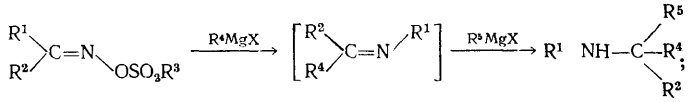
The partial rate constants for parallel reactions are greatly influenced by the basicity of the solvent, whose increase as a rule entails a decrease in the above quantities.[45]

Later studies[46,47] of the interaction of ketones with Grignard reagents confirmed the validity of the conclusions reached by Khyrak et al.[45]

Thus the reactions of organomagnesium compounds with ketones (and other carbonyl compounds) proceed via at least three independent pathways examined above. The yield of the products in each pathway is not related to the structures of the ketone and the Grignard reagent. This feature is reflected in the partial rate constants.

Many reactions of organomagnesium compounds involving major internal rearrangements of the substrate have now been discovered. These reactions are not characteristic of organolithium compounds and cannot be understood from the standpoint of reactions of the second type (nucleophilic substitution). These reactions are determined by the Lewis acid properties of RMgX.

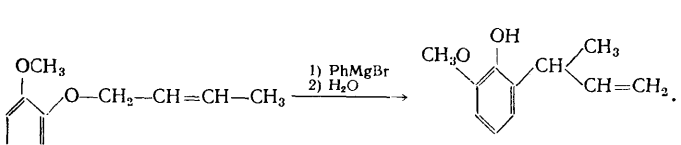
(b) The Lewis acid properties of organomagnesium compounds. Before discussing specific reactions involving the heterolysis of C–element σ-bonds, we should like to quote a number of examples of the behaviour of the Grignard reagent as a typical electrophile. The Beckmann rearrangement of oxime sulphonates has been discovered.[48] It takes place on treatment with organomagnesium compounds:



$R^4MgX = CH_3MgI$, n-$C_4H_9C{\equiv}CMgBr$.

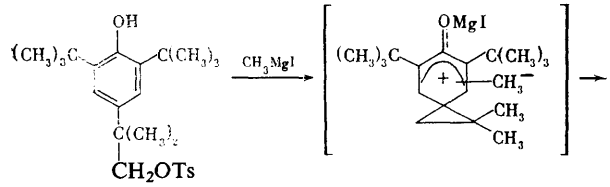
The imines formed are converted under the influence of the excess R_5MgX into secondary amines. Neither the nature of the organic group nor that of the halogen influences significantly the rearrangement.

Another example illustrating strikingly the Lewis acid properties of a Grignard reagent may be the Claisen rearrangement of the ether shown below under the influence of phenylmagnesium bromide:[49]

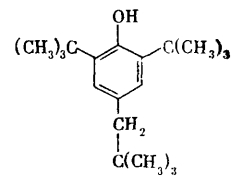


23%

It is believed that phenyl tosylate also undergoes a rearrangement on treatment with a Grignard reagent and it is assumed that the latter proceeds via a pyrocyclic complex:



Ts = *n*-$CH_3C_6H_4SO_2$–



The question of the existence of the complex is apparently controversial but presumably a carbonium-like transition state may be formed on treatment with RMgX.

Thus organomagnesium compounds, acting on certain substrates as Lewis acids, can induce profound changes in their molecular skeleton.

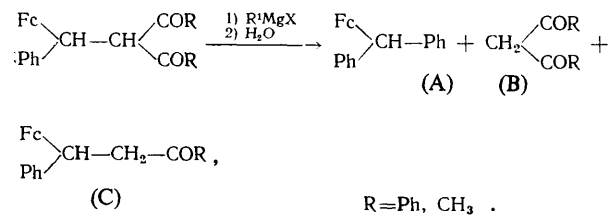
The data described below are devoted to the analysis of the characteristics of the structures of the substrate and the reagent necessary for the fragmentation of σ-bonds under the influence of the Grignard reagent.

III. Reactions involving the heterolysis of carbon–element α-bonds by Grignard reagents

1. C–C heterolysis

σ-C–C heterolysis on treatment with RMgX is not by itself a very interesting reaction, since in the given instance a very strong bond is usually readily fragmented. The authors of the present review studied this reaction in detail in relation to β-dicarbonyl compounds and discovered its principal characteristic features which made it possible to regard σ-C–C heterolysis as a special case of the more general fragmentation of the C–element σ-bond by organomagnesium compounds and other Lewis acids. We therefore decided to begin the consideration of the problem indicated in the heading of this Section with the cleavage of a C–C σ-bond.

The interesting reaction involving the fragmentation of a C–C σ-bond in ferrocene-containing β-diketones by Grignard reagents was discovered in 1980 (Table 2):[51,52]



(A) (B) (C)

R=Ph, CH_3 .

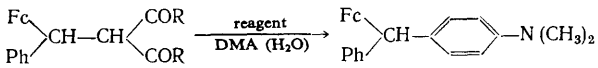
Together with the C–C cleavage products, traces of the ketone cleavage products were detected. The difference between the yields of the σ-C–C fragmentation products has been explained[51,52] by the difference between the nucleophilic properties of the Grignard reagents.

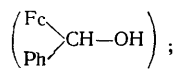
Table 2. The yields of the products of the reactions of RMgX with β-diketones.

R	Reagent	Yield of products, %			Refs.
		(A)	(B)	(C)	
CH_3	PhMgBr	35	см.*	см.*	[51]
CH_3	CH_3MgI	17	см.*	см.*	[52]
Ph	PhMgBr	60	74	insignificant	[53]

*Not isolated.

In another study,[53] the same workers showed that ferrocene-containing β-diketones are cleaved at a C–C σ-bond by strong Lewis acids: $MgBr_2$, $ZnCl_2$, $SnCl_4$, as well as trifluoroacetic acid:

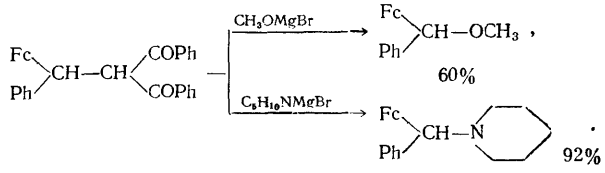




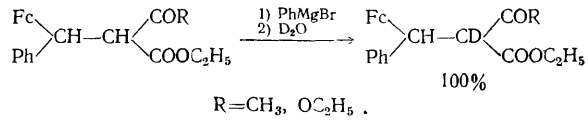
; DMA = dimethylaniline .

According to the authors[52,53] the nature of the cleavage by RMgX and by strong Lewis acids is different.

The nature of the interaction of α-monosubstituted β-dicarbonyl compounds with Grignard reagents was studied in detail by the present authors.[54] In the first place, we established that the Lewis acid properties of RMgX are in fact responsible for the σ–C–C fragmentation. This conclusion follows from the following observations: firstly, an increase in the solvating capacity of the solvent led to a sharp increase in the yield of the product of the fragmentation considered, as far as its complete disappearance from the reaction mixture in the presence of crown-ethers, and, secondly, in contrast to lithium piperidide and alcoholic alkali, dibenzoyl-(ferrocenylphenylmethyl)methane is cleaved by piperidylmagnesium bromide and methoxymagnesium bromide:[55]



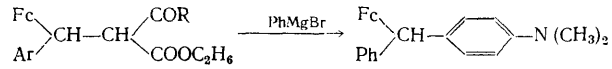
It has also been established that this reaction depends on the structure of the β-dicarbonyl component of the substrate. In contrast to β-diketones, a β-ketoester and diester are not cleaved by phenylmagnesium bromide at a C–C σ-bond. In this case, the enolisation of the β-dicarbonyl compound takes place quantitatively:



;

R=CH_3, OC_2H_5 .

The σ-C–C fragmentation depends in many respects on the stability of the carbonium ion, which can be formed by the α-substituent. *p*-Dimethylaminophenylferrocyenylmethylmalonic and acetoacetic esters are cleaved at a C–C σ-bond:[56]

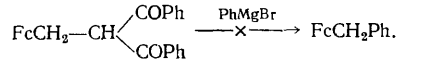


;

Ar=*n*-$(CH_3)_2NC_6H_4$

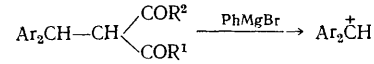
R=CH_3 (83%),
R=OC_2H_5 (7%).

On the other hand, as a result of a decrease in the stability of the carbonium ion formed by the α-substituent, dibenzoyl-(ferrocenylmethyl)methane is not fragmented by phenylmagnesium bromide:[57]



Thus we reached the following conclusions: the course of the σ-C–C cleavage reaction is determined by the stability of the carbonium ion formed by the α-substituent of the substrate and also by the stability of the carbanion formed by the unsubstituted β-dicarbonyl compound, the role of the Lewis acid properties of the organomagnesium compound being decisive.[57,59] The σ-C–C fragmentation reaction should therefore be characteristic also of compounds without the ferrocenyl fragment and also not only of β-dicarbonyl compounds.

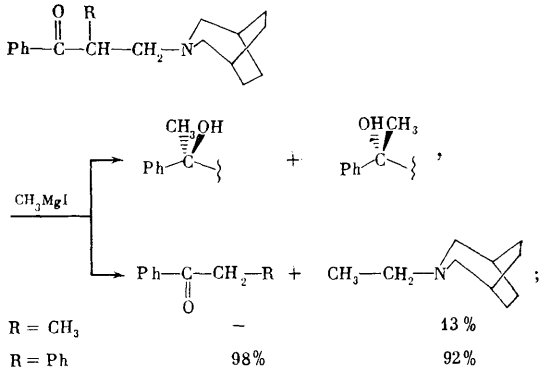
The reaction under discussion has been observed, for example, with derivatives of bis(*p*-dimethylaminophenyl)methyl series:[60]



R^1=R^2=CH_3, Ph, OC_2H_5;
R^1=CH_3, R^2=OC_2H_5.

The occurrence of fragmentation was inferred from the appearance of the λ_{max} = 611 nm band characteristic of bis(*p*-dimethylaminophenyl)methyl carbonium ion.[61]

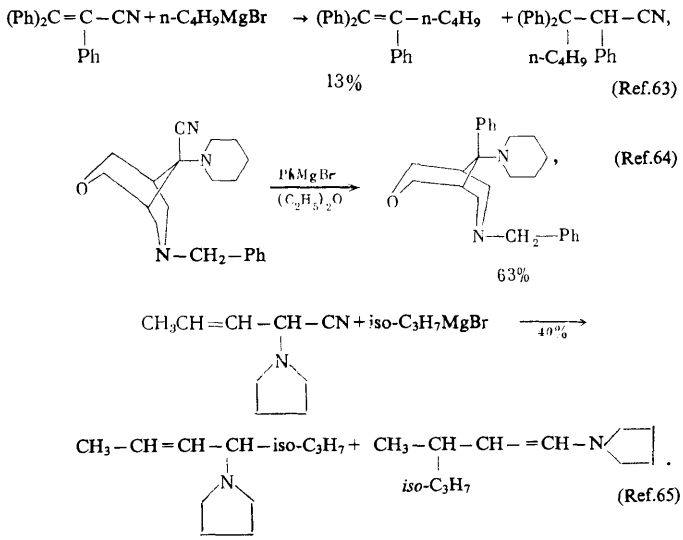
It has been established[62] that the σ-C−C fragmentation reaction also takes place with certain monocarbonyl compounds:



R = CH_3	–	13 %
R = Ph	98%	92%

This "anomalous" reaction, in the view of Angiolini et al.,[62] is accompanied by the "normal" nucleophilic addition reaction.

The σ-C−C cleavage reaction has been observed[63–65] for nitrile derivatives:



(Ref.63)

(Ref.64)

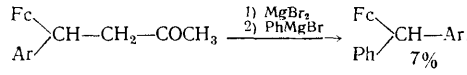
(Ref.65)

In all the studies examined above, the σ-C−C cleavage reaction is accompanied by addition to the nitrile group[64,65] (1,2-addition) and to alkene double bond (1,4-addition).[63]

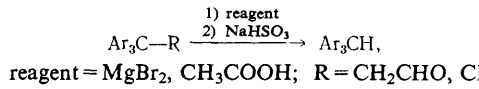
Thus the σ-C−C fragmentation of organic compounds by Grignard reagents is one of the possible reaction pathways, provided that (1) the substrate molecules can be imagined to be cleaved into a stable carbonium ion and a carbanion (the stability of the fragment is correlated with the values of pK_{R^+} and pK_a for the carbonium ion formed by the α-substituent and the carbanion derived from the unsubstituted β-dicarbonyl compound respectively) and (2) the strength of the Lewis acids RMgX must be sufficient for the fragmentation of the substrate molecule.

The σ-C−C dissociation reactions are obscured by parallel reactions involving addition to the carbonyl group and enolisation. This apparently leads to a complex dependence of the yield of the σ-C−C cleavage products on the Lewis acidity of the organomagnesium compounds expressed in terms of φ*.[12]

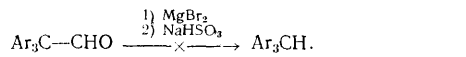
This obstacle can be avoided using strong Lewis acids or protic acids. Thus, although monocarbonyl compounds are not fragmented by a Grignard reagent, they are cleaved at a C−C σ-bond by magnesium bromide etherate:[54]



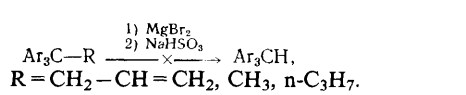
Aldehydes, nitro-compounds, and the nitrile oxides of the tris(*p*-dimethylaminophenyl)methyl series undergo σ-C−C fragmentation:[66–68]



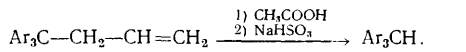
Although the authors[66–68] do not explain the observed phenomenon, it can be understood in terms of the values of pK_{R^+} and pK_a. The relation between these quantities, estimated in terms of pK_a and pK_{R^+}, can be demonstrated by the following example. Despite the high thermodynamic stability of $Ar_3\overset{+}{C}H$, compounds forming unstable carbanions are not cleaved:[66]



The primary coordination of the reagent and the substrate is extremely important for the σ-C−C fragmentation reaction. This postulate is well illustrated by the following example:[68]



On formation of two stable ions, the possibility of the protonation of the olefinic double bond by acetic acid appears, which leads to the σ-C−C fragmentation of tris(*p*-dimethylaminophenyl)methylallyl:[68]



The ready fragmentation of β-dicarbonyl compounds of the bis(*p*-dimethylaminophenyl)methyl series at a C−C σ-bond by acetic acid, discovered in 1909 by Fosse,[698] also becomes entirely explicable:

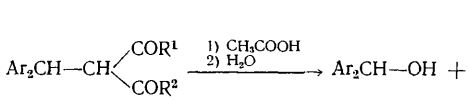
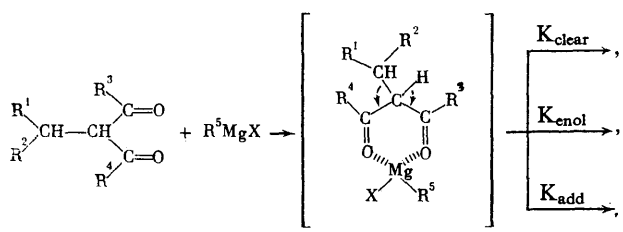


Table 3. The yields of the products of the cleavage of ethers.

No.	Substrate	Reagent	Yield of products, %		Refs.
			(D), (D′)	(E), (E′)	
1	Ph–CH=CH–CH_2–O–$(CH_2)_2$Ph	n-C_6H_{13}MgBr	Ph, n-C_6H_{13} >CH–CH=CH_2 15	Ph$(CH_2)_2$OH 23	[76]
2	PhCH=CH–CH_2–O–C_4H_9	n-C_7H_{15}MgBr	Ph, n-C_7H_{15} >CH–CH=CH_2 52	n-C_4H_9OH 76	[77]
3	CH_2=CH–CH_2–O–Ph	PhMgBr	Ph–CH_2–CH=CH_2 30	PhOH 60	[77]
4	CH_3–CH=CH–CH(t-C_4H_9)–O–$C(CH_3)_3$	n-C_8H_{17}MgBr	CH_3–CH(n-C_8H_{17})–CH=CH–$C(CH_3)_3$ 62	$(CH_3)_3$COH 88	[78]

The following mechanism has been proposed for the σ-C–C fragmentation of β-dicarbonyl compounds (different classes of organic compounds) by Grignard reagents (and other Lewis acids):[54]



In the first stage of the reaction, the β-dicarbonyl compounds is coordinated to the Grignard reagent (chelate formation).[70] It is well known that the coordination of Lewis acids, especially of the Mg^{2+} ion,[71] labilises the proton in the α-position relative to the carbonyl group.[72] When the molecule contains an α-substituent capable of giving rise to a stable carbonium ion, the α-substituent begins to compete with the proton as regards lability, i.e. the σ-C–C cleavage and enolisation reactions complete, whereupon the coordination of the reagent enhances also the electrophilic properties of the carbonyl groups.

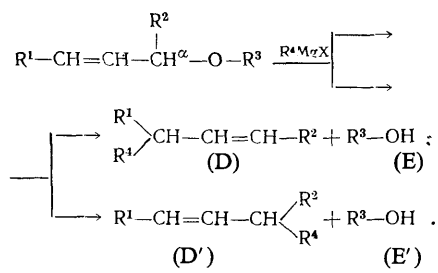
Thus coordination (chelate formation[73,74]) of the Grignard reagent leads to polarisation (in extreme cases to ionisation) of the C–C, C–H, and C=O bonds, which are in any case already polarised.[75] In the second stage, the three cryptobasic centres formed are attacked with different effectiveness. The ratio of the products via the three pathways — σ-C–C cleavage, enolisation, and addition of the carbonyl group — depends on the ratio of the partial constants K_{cleav} (cleavage) K_{enol}, and K_{add}.

The characteristics noted for the σ-C–C fragmentation of β-dicarbonyl and monocarbonyl compounds hold also for other classes of organic compounds.

2. C–O Heterolysis

(a) The cleavage of ethers. A number of ethers undergo heterolysis at a C–O σ-bond on treatment with Grignard reagents. This reaction is observed only for a particular structure of organic compounds of this class.

Vinyl and allyl ethers undergo cleavage at a C–O σ-bond. The observed reaction can be represented schematically in the following manner in relation to αβ-unsaturated ethers:



Data on the σ-C–C heterolysis of unsaturated ethers are compiled in Table 3.

By analogy with ketones, it is believed,[77,78] that a complex of the Grignard reagent with the ether is formed initially and then rearranges with formation of the products of the given reaction. Hill et al.[77] believe that the coordination of the RMgX molecule to that of the ether increases the electron density deficiency on the α-carbon atom with subsequent attack on the latter by the cryptobase (1,2-addition). The 1,4-adducts are consistent with the mechanism involving a six-membered transition state.[77]

On the other hand, the authors themselves[76,78] noted that the model with the six-membered state is not universally applicable to the given reaction, since it does not explain the composition of the products of the reaction of RMgX with ethers having bulky substituents in the 2- or 4-position (Table 3, example 4).

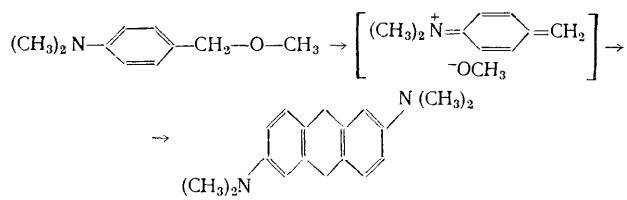
We may note that the molecules of unsaturated ethers, presented in Table 3, can be cleaved into two fragments: the stable allylcarbonium ion and the alkoxide (enolate) anion.

The presence of the carbonium ion in the transition state explains satsifactorily the presence in the reaction mixture of the products of the Claisen isomerisation of the enol ether. The presence in the molecule of a group which can be readily eliminated makes possible the cleavage at a C–O σ-bond of the tosylate derived from a sterically hindered enol (see above).

As in σ-C–C heterolysis, the coordination of RMgX to the oxygen atom of the ether leads to intense polarisation (ionisation) of a C–C σ-bond and attack by the nucleophilic completes the heterolysis.

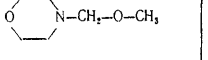
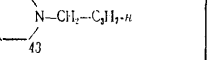
The data presented in Table 4 may serve as evidence in support of the occurrence of the reaction investigated via an ionic mechanism.

The existence of immonium structures in the transition state has been postulated.[79] According to these workers, this explains the presence of condensed systems in the reaction mixture:



The immonium ion was formed not under the influence of RMgX, but, as follows from the mechanism proposed by the authors,[79] resulted from σ–σ conjugation.

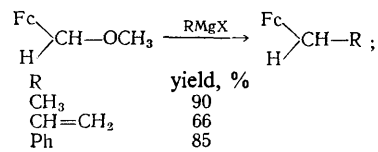
Table 4. Yields of the products of the cleavage of ethers.

No.	Substrate	Reagent	Yield of product, %	Refs.
1	Ar–CH_2–O–CH_3	PhMgBr	Ar–CH_2–Ph 84	[79]
2		**n-C_3H_7MgBr**	 43	[80]
3	$(CH_3O)_2CH$–$N(CH_3)_2$	PhMgBr	$(Ph)_2CH$–$N(CH_3)_2$ 89	[81]
4	PhO–$CH(OC_2H_5)_2$	**n-C_4H_9MgBr**	**n-$C_4H_9CH(OC_2H_5)_2$** 90	[82]
5	CH_3O–CH_2NR_2	$(CH_3)_3SiCH_2MgCl$	$(CH_3)_3SiCH_2$–CH_2NR_2 70	[83]
6	PhOCH$(OC_2H_5)_2$	CH_2=CH–CH_2MgBr	CH_2=CH–CH_2–$CH(OC_2H_5)_2$ 70	[84]
7	$(PhO)_2CHOC_2H_5$	**n-C_4H_9MgBr**	$(C_4H_9)_2CHOC_2H_5$ 74	[85]
8	(PhO)$CH(OC_2H_5)_2$	**n-C_4H_9MgBr**	**n-$C_4H_9CH(OC_2H_5)_2$** 80	[86]
9	$CH_3OCH_2N[Si(CH_3)_3]_2$	CH_3MgBr	$CH_3CH_2N[Si(CH_3)_3]_2$ 89	[87]

The C–O σ-bond in the ethers listed in Table 4 is so labile that, in contrast to the compounds listed in Table 3, the σ-C–O heterolysis by organomagnesium compounds in THF of ethers, which are cleaved in diethyl ether or diethyl ether–benzene mixtures, takes place with high yields.

In all the examples listed in Table 4, the C–O σ-bond is cleaved selectively — on the side of the most stable immonium cation. On the other hand, when the molecule contains carbonium ions of comparable stability, cleavage takes place on the side of the more stable anion (Table 4, examples 4 and 6–8).

There is nothing surprising about the fact that the ethers containing the ferrocenyl group — a powerful stabiliser of the α-carbonium ion — undergo σ-C–O heterolysis by organomagnesium compounds:[88]

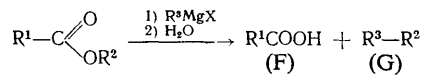


R	yield, %
CH_3	90
$CH=CH_2$	66
Ph	85

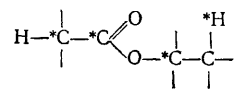
In this case, the σ-bond under consideration is highly polarised (ionised) and coordination of RMgX leads to σ-C–O fragmentation in the presence of a leaving group which is effectively eliminated.

Thus ethers are selectively cleaved at a C–O σ-bond, the latter being fragmented on the side where stable carbonium ions and alkoxides are formed.

(b) The cleavage of esters. A number of esters undergo σ-C–O fragmentation on treatment with RMgX:



At least three parallel reactions take place simultaneously due to the existence of the following four reaction centres:[89]

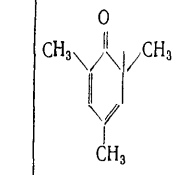
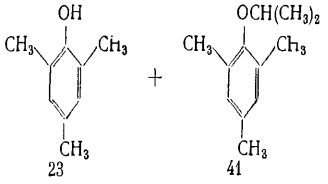


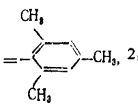
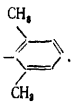
All the possible reaction pathways operate after the formation of the coordination complex of RMgX and the substrates as a result of its rearrangement.[90] The reaction with a six-membered transition state has been postulated[91,92] as anomalous for σ-C–O heterolysis. In a later study,[93] the mechanism with a six-membered transition state was questioned and an ionic reaction mechanism was put forward for the reaction with the following characteristic features: (1) the alkyl substituent linked to the oxygen atom is capable of giving rise to a stable carbonium ion; (2) among the ethoxycarbonyl groups, the "normal" addition to the carbonyl group is hindered and is therefore retarded.

Table 5 presents a compilation of data on the σ-C–O heterolysis of esters.

The postulates of Arnold and Searles[93] are applicable in cases 2, 3, 6, and 7 (Table 5), while in other instances they fail to account for the occurrence of σ-C–O heterolysis. Indeed, in examples 1, 4, 5, 8, and 9, the ethoxycarbonyl group is not blocked to nucleophilic attack by the cryptobase, but the cleavage under consideration does not occur.

Table 5. The yields of the products of the cleavage of esters.

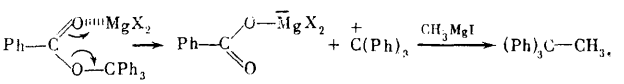
No.	R^1	R^2	Reagent	Yields of products, % (F)	Yields of products, % (G)	Refs.
1	Ph	$CH_2-CH=CH_2$	Mes*MgBr	Mes$-CH_2-CH=CH_2$ 57	PhCOOH 26	[90]
2	$PhCH_2$, CH_3-C, C_2H_5	$CH_2-CH=CH_2$	PhMgBr	$Ph-CH_2-CH=CH_2$ 70	$PhCH(CH_3)(C_2H_5)-C(-)-COOH$ 87	[92]
3	Mes	$C(CH_3)_3$	PhMgBr	$Ph-C(CH_3)_3$ 24	MesCOOH 9	[93]
4	CH_3	$C(Ph)_3$	$(CH_3)_3CMgCl$	$(Ph)_3C-C(CH_3)_3$ 20 + $(Ph)_3C-H$ 10	2*	[94]
5	Ph	$CH(Mes)_2$	C_2H_5MgBr	$(Mes)_2CH-C_2H_5$ 32 + $(Mes)_2CH_2$ 12	PhCOOH 9	[95]
6	Dur[3*]	$CH_2CH=CH_2$	PhMgBr	$Ph-CH_2-CH=CH_2$ 70	DurCOOH 35	[96]
7	Mes	$CH_2-CH=CH-CH_3$	PhMgBr	$Ph(CH_3)CH-CH=CH_2$ 58 + $Ph-CH_2-CH=CH-CH_3$ 12	2*	[97]
8	CH_3	$C(Ph)_3$	CH_3MgBr	$(Ph)_3C-CH_3$ 68	2*	[98]
9	CH_2		$(CH_3)_3CMgBr$	 23 + 41	2*	[99]

Mes =  , [2] Not isolated. [3]* Dur =  .

The occurrence of cleavage in case 5 is inexplicable from the standpoint of these two postulates. Firstly, the carbonyl group of the ester is fairly active in nucleophilic addition reactions and, secondly, the dimesityl carbonium ion is apparently unstable.[98] It is sufficient to note that, according to the data of Fieser and Heymann,[98] neither diphenylmethyl acetate nor fluorenyl acetate are cleaved by phenylmagnesium bromide at the C–O σ-bond.

In the given instance, the stability of the leaving group assumes an important role in our view: $K_a = 1.75 \times 10^{-5}$ for CH_3COOH and $K_a = 6.5 \times 10^{-5}$ for PhCOOH. Incidentally, one cannot rule out also an important contribution by the *I* effect of the methyl group to the stability of the dimesityl carbonium ion.

It is important to note that both in the original studies[89–99] and in the monographs referring to these investigations, in the interpretation of the σ-C–O cleavage of esters by RMgX the authors invoke the Lewis acid properties of magnesium bromide etherate:[100]



The examination of the structure of RMgX in the earlier part of the review showed that even at high dilutions the content of MgX_2, formed in accordance with the Schlenk equilibrium in ethereal solutions and in other weakly solvating solvents, where the heterolysis under consideration takes place, is extremely insignificant. The formation of magnesium halides as a result of the reaction analogous to the Wurtz reaction, occurring simultaneously with the formation of asymmetric and symmetrical organomagnesium compounds, is unlikely.[101]

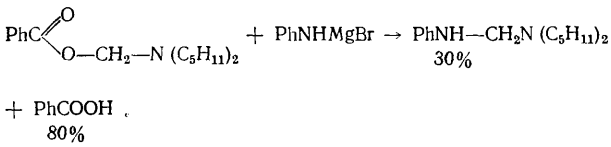
Under the experimental conditions (ethereal solution, $c > 0.01$ M), polyassociated species always exist and the MgX_2 formed therefore forms part of the composition of these macromolecular formations, its acid properties being weakened under these conditions.

In the case of organomagnesium compounds with branched alkyl groups (Table 4, example 4), a reduction reaction is observed together with the nucleophilic substitution reaction. In our view this is associated with the fact that, on coordination to the ester molecule via the C—O σ-bond, RMgX is highly polarised to such an extent that attack on the new electrophilic centre becomes possible not only by R^- but also by the hydride ion.

The presence of 1,2- and 1,4-adducts derived from allyl esters can be readily accounted for from the standpoint of a carbonium-like transition state, while the mechanism with a six-membered transition state and a synchronous redistribution of electrons does not explain it—for example in case 7 in Table 5.

Thus the σ-C—O cleavage reaction can be observed or not observed for esters with a bulky substituent R^1, i.e. the steric hindrance to nucleophilic addition via the carbonyl group generated by this substituent is not obligatory or of decisive importance for the reaction considered. On the other hand, the σ-C—O heterolysis may be expected if the substituent R^2 is capable of forming stable carbonium ions. The influence of the structure of R^3 on the cleavage considered is expressed by the fact that, together with the cleavage products (G) (in the scheme above), one may expect also the reduction products (H-R_2) in the case of branches groups R_3, and is also reflected by the contribution resulting from the Lewis acidity, expressed, for example, in terms of φ * (see above).

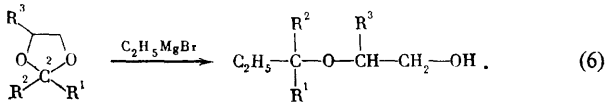
The nucleophilicity of the Grignard reagent is apparently unimportant for the heterolysis reaction, since esters are cleaved by various organomagnesium compounds. The cleavage of esters by RNHMgX has been described:[102,103]



The C—O fragmentation involving ethers and R_2NMgX takes place similarly.[104]

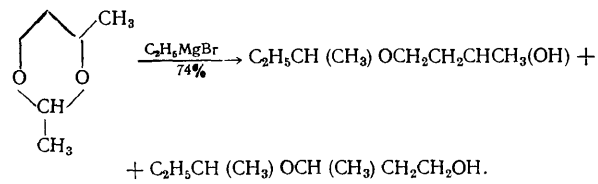
Thus the heterolysis examined above is analogous to the reaction involving ethers and is determined by the stability of the carboxylate ions and carbonium ions which can be formed by the substituent R^2. The role of the Lewis acid properties of RMgX is then decisive.

(c) The cleavage of 1,3-dioxolans. Cyclic ketals and acetals undergo the σ-C—O heterolysis on treatment with organomagnesium compounds. This reaction proceeds as a rule under more severe conditions than those examined above—in boiling benzene or toluene:[105]



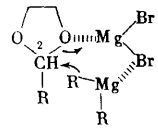
(6)

Dioxolans forming six-membered rings are cleaved under still more severe conditions than the five-membered compounds. This is believed[105] to be associated with the smaller strain in six-membered rings:



Data on the σ-C—O heterolysis of 1,3-dioxolans are compiled in Table 6.

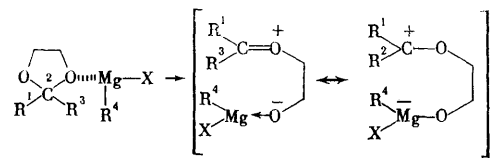
The mechanism of σ-C—O heterolysis involving a six-membered transition state was postulated in almost all the studied presented in Table 6:



It has been suggested[106–110] that the driving force of the σ-C—O heterolytic process is the polarisation of the cleaved C—O bond by magnesium bromide etherate. The cleavage process is regarded as a concerted circular electron transfer. According to the authors,[106–110] this mechanism is confirmed by the isolation of the complexes of 1,3-dioxolans with MgX_2 (2,4-dimethyl-1,3-dioxolan : MgX_2 = 1.65 : 1).

In their assessment of the influence of substituents in the 2-position on the ease of opening of the dioxolan ring, Trofimov et al.[108] noted the parallel variation of the yield of the products of σ-C—O heterolysis and the electron-donating capacity of the substituents (for example, the unsubstituted dioxolan is not cleaved by RMgX). However, the observed variation has not been explained.[106–110]

Blomberg et al.[111] explained the influence of the substituents in the 2-position in the dioxolan molecule by the fact that the mesomeric form of the transition state includes the C(2)-carbonium ions, which is stabilised by electron-donating substituents.



In a later study,[114] it was suggested that the interaction of a series of dioxolans with Grignard reagents results in the formation of an oxocarbonium transition state and that the driving force of the process is the Lewis acid properties of all the organomagnesium conglomerates present in solution: the RMgX monomers at a low concentration and the $(RMgX)_n$ polymers at a high concentration:

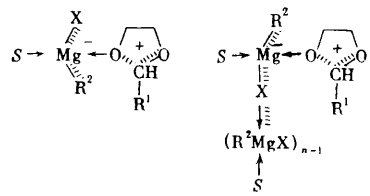
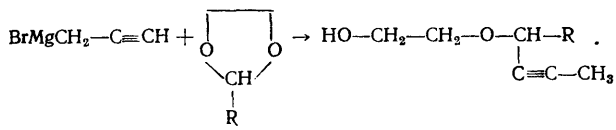


Table 6. The yields of the products of the cleavage of dioxolans via reaction (6).

No.	R^1	R^2	R^3	Reagent	Yield of product, %	Refs.
1	CH_3	H	H	$CH_2=CH-C\equiv CMgBr$	$CH_2=CH-C\equiv C-CH(CH_3)-O-(CH_2)_2OH$ 58	[106]
2	CH_3	H	CH_3	C_2H_5MgBr	$(C_2H_5)(CH_3)CH-O-CH(CH_3)(CH_2OH)$ 54	[107]
3	CH_3	C_2H_5	H	$CH_3CH_2-C\equiv CMgBr$	$CH_3-CH_2-C\equiv C-C(CH_3)(C_2H_5)-O-(CH_2)_2OH$ 80	[108]
4	CH_3	H	H	$PhC\equiv CMgBr$	$PhC\equiv C-CH(CH_3)-O-(CH_2)_2OH$ 67	[109]
5	CH_3	C_2H_5	CH_3	$BrMgOCH_2C\equiv CMgBr$	$HO-CH_2-C\equiv C-C(CH_3)(C_2H_5)-O-CH(CH_3)-CH_2-OH$ 75	[110]
6	$n\text{-}C_3H_7$	H	H	C_2H_5MgBr	$(n\text{-}C_3H_7)(C_2H_5)CH-O-CH_2-CH_2OH$ 78	[111]
7	CH_3	$-CH(SCH_3)-CH_2-CH_3$	H	$CH_2=CH-C\equiv CMgBr$	$CH_2=CH-C\equiv C-C(CH_3)(CH_2-CH_2-OH)(CH-CH_3SCH_3)$ 53	[112]
8	H	CH_3	CH_3	$(CH_3)_2CHMgBr$	$(CH_3)_2CH-CH(CH_3)-O-CH(CH_3)-CH_2OH$ 71	[113]

In a study[115] of the σ-C–O cleavage of a dioxolan by a Grignard reagent, the formation of the final reaction product was attributed to the nucleophilic properties of RMgX and its structure was attributed to the migration of the triple bond under the influence of the base and temperature:



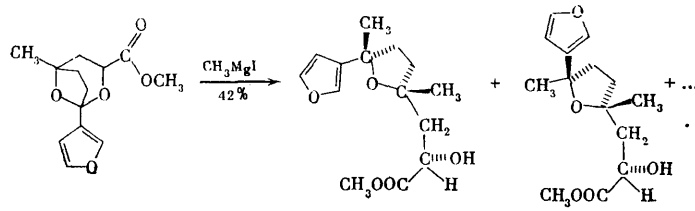
We believe that, firstly, in the given case σ-C–O heterolysis takes place and, secondly, that the above workers[115] indicate an erroneous structure of the reagent.

In view of the greater basicity of a carbanion with an sp^3-hybridised carbon atom than that of a carbanion with an *sp*-hybridised carbon atom,[116] the structure of the reagent can be represented by the formula $CH_3-C\equiv CMgBr$.

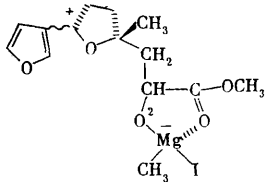
The following equilibrium may be established in solution:

$$CH_3C\equiv CMgBr \rightleftarrows BrMgCH_2-C\equiv CH.$$

Abell and Mass-Westropp[117] observed the heterolytic cleavage of the C–O σ-bond in dioxolan:

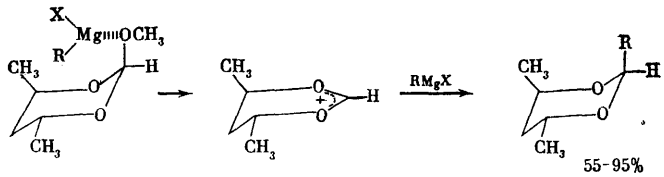


The selectivity of the reaction, reflected in the products, can be explained according to the authors[117] by the chelation reaction of the methoxycarbonyl group, via the O(2) atom, with methylmagnesium iodide and the subsequent formation of an oxocarbonium ion:

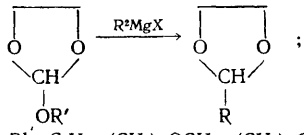


A competing reaction involving nucleophilic addition to the carbonyl group takes place simultaneously. The relation between the stabilities of the two fragments produced as a result of the breakup of the dioxolan molecule after coordination was not investigated in the above study.

The stereospecific synthesis of 1,3-dioxolans with an axial substituent at the C(2) atom has been described:[118]



This character of the reaction is determined, according to the authors,[118] by the need for a stereoelectronic factor in the formation and subsequent reaction of the oxocarbonium ion. It has been shown[119] that at high temperatures cyclic ortho-esters are cleaved by Grignard reagents also in a highly basic solvent—tetrahydrofuran



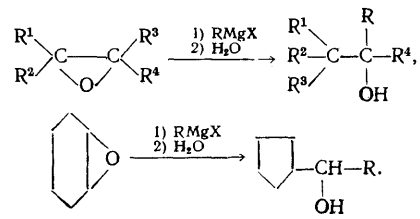
$R^1 = C_2H_5$, $(CH_2)_2OCH_3$, $(CH_2)_2O(CH_2)_2OCH_3$.

The driving force of the above process is believed[119] to be the coordination of MgX_2 to the oxygen atom linked directly to the C(2) atom. An increase in the number of oxygen atoms in the substituent R leads to a fall in the yield of the product of σ-C—O heterolysis owing to the saturation of the coordination sites of magnesium by the oxygen atoms of the substituent R^1 remote from the C(2) atom (i.e. owing to the weakening of the Lewis acid properties of the Grignard reagent).

Thus the σ-C—O heterolysis of 1,3-dioxolans by RMgX is one of the examples of the fragmentation of substrates by a Lewis acid. This reaction proceeds if a stable carbonium ion can be generated in the dioxolan molecule under the influence of RMgX. An alkoxide ion is invariably the leaving group. The acceleration of the heterolysis by the introduction of electron-donating substituents in the 2-position occurs, in our view, as a result of the stabilisation of the carbonium ion in the transition state. The introduction of alkoxy-substituents, i.e. effective leaving groups, into the 2-position in cyclic ortho-esters leads to the formation of 1,3-dioxolans.

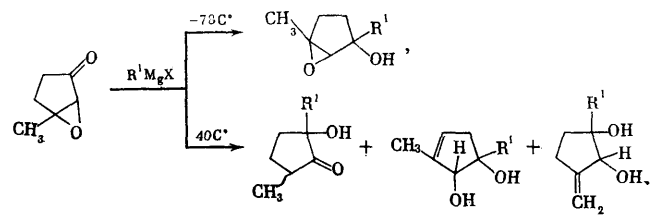
The marked dependence on the solvating capacity of the solvent and the uncharacteristic course of the σ-C—O heterolysis of organolithium compounds show that the Lewis acid properties of RMgX in the reaction under discussion are responsible for the possibility of the occurrence of the σ-C—O heterolysis of dioxolans.

(d) Isomerisation of epoxides. Organomagnesium compounds induce the isomerisation of epoxides similarly to the Lewis acids MgX_2:[120–125]



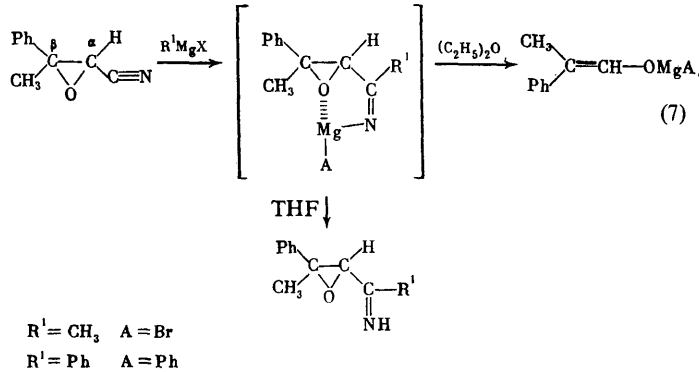
The above isomerisation reaction is accompanied, according to the authors,[122–125] by the simultaneous "normal" nucleophilic opening of the ring. The isomerisation of epoxides by organomagnesium compounds is fully inhibited in highly basic solvents.

It is sometimes possible to isolate the epoxide isomerisation products themselves. An α-hydroxyketone has been identified[126,127] in the reaction mixture produced by the interaction of α-epoxycyclopentanones with RMgX:



The above scheme shows that the products of the reaction are determined by the temperature of the reaction mixture. An increase in temperature enhances the acid properties, i.e. leads to isomerisation.

The species inducing the isomerisation of certain epoxides are alkyl(aryl)magnesium imines:[128–130]

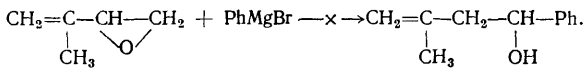


(7)

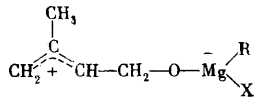
$R^1 = CH_3$ A = Br
$R^1 = Ph$ A = Ph

Scheme (7) shows that the acid properties of magnesium-containing conglomerates are responsible for the possibility of isomerisation.

The cleavage of isopropenyloxiran by phenylmagnesium bromide has been investigated,[131] but the epoxide isomerisation products were not detected in the reaction mixture:



In our view, in the given instance a carbonium-like state with a primary carbon atom is not produced because of the higher stability of a carbonium-like transition state with a secondary carbon atom stabilised by $\pi-\pi$ conjugation:



We believe that isomerisation proceeds because the epoxide molecule can be cleaved into two stable oppositely charged fragments within the molecule, which rapidly and irreversibly isomerise to ketones or aldehydes. The carbonyl compounds formed combined with an RMgX molecule and are converted into carbinols.

(e) The cleavage of carbinols and alkoxides. After introduction with RMgX in weakly solvating solvents, many ketones form the products of the "anomalous" reaction: after the "normal" addition to the carbonyl group, the magnesium alkoxide formed reacts with another RMgX molecule and is cleaved at the C–O σ-bond[132–137] (Table 7):

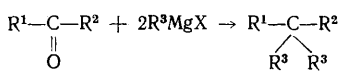
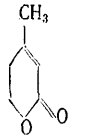
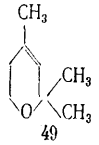
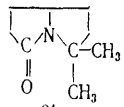
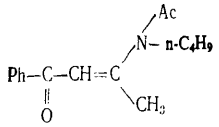
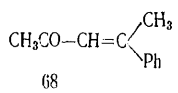
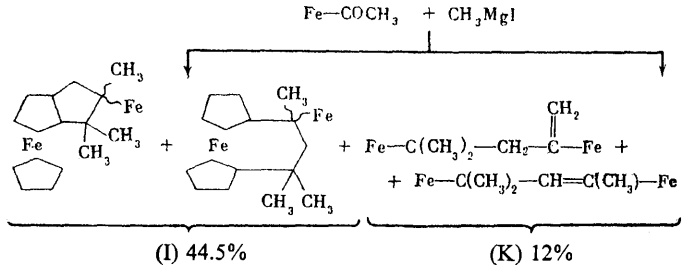


Table 7. The yields of the products of the cleavage of carbinols and alkoxides.

Substrate	Reagent	Yield of product, %	Refs.
	CH_3MgI	 49	[132]
	CH_3MgBr	 21	[133]
	CH_3MgI	 68	[134]
	RMgX		[135]
$FcC(CH_3)_2OH$	CH_3MgI	$FcC(CH_3)_2$ 14	[136,137]

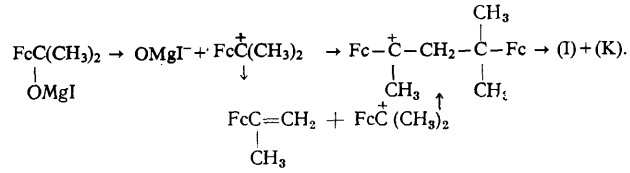
All the substrates listed in Table 7 contain in the α-position relative to the carbonyl carbon atom potential stabilisers of the α-carbonium ion—nitrogen and oxygen atoms and the ferrocenyl group. On the other hand, the oxygen ion stabilised by the MgX^+ counterion is converted into a readily eliminated group and thus the lability of the C–O σ-bond in such alkoxides becomes understandable.

The isolation of products of the intramolecular homo- and heteroannular alkylation of the ferrocenyl substituent and also of ferrocene-containing alkenes from the reaction mixture produced by the interaction of acetylferrocene and methylmagnesium iodide supports the view that the reactions of the organic compounds of the classes considered proceed via a stage in which a carbonium ion (a carbonium-like transition state) is formed:



(I) 44.5% (K) 12%

It is believed[136,137] that the reactions discussed above proceed via the C–O σ-bond ionisation stage with formation of the dimethylferrocenylcarbonium ion:



3. The cleavage of the C–Cl bond

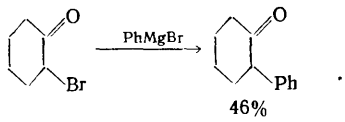
Certain chlorine-containing compounds undergo heterolysis at the C–Cl σ-bond by Grignard reagents. Table 8 presents examples of such reactions.

It is striking that all the cleaved compounds can give rise to a stable carbonium ion and a stable anion and that, in the presence of two chlorine atoms in the substrate molecule (two readily eliminated groups) (Table 8, examples 1 and 6), the $C^{\alpha}-Cl^{\beta}$ σ-bond is cleaved (Table 8, example 1).

Arbuzov et al.[138] noted that the stereochemical results of the interaction of 2,3-dichlorotetrahydropyran with RMgX can be explained by the intermediate formation of an oxocarbonium ion.

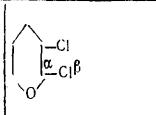
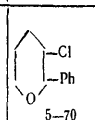
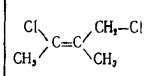
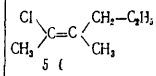
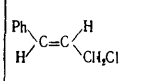
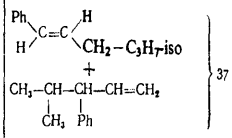
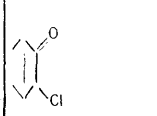
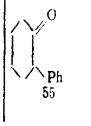
It has been noted[142] that the substitution of the chlorine atom in (*Z*)-3-chloro-1-phenylpropene takes place only in ether; in THF, the products of the C–Cl heterolysis—(*Z*)-4-methyl-1-phenylpent-1-ene and (*Z*)-4-methyl-3-phenylpent-1-ene—are not formed. Although this fact was not explained,[142] we believe that in the given instance the weakening of the Lewis acid properties of RMgX in THF prevents the fragmentation of the chlorine-containing alkene.

Grignard reagents also cleave bromine-containing compounds. The cleavage of the C–Br σ-bond has been described:[140]



Apparently iodine- and fluorine-containing compounds can also be cleaved by RMgX.

Table 8. The yields of the products of the cleavage of chlorine-containing compounds.

No.	Substrate	Reagent	Yield of product, %	Refs.
1		PhMgBr	 5–70	[138–140]
2		C_4H_9MgBr	 5 (	[141]
3		iso-C_3H_7MgB	 37	[142]
4	$CH_3CH{=}C(Cl){-}CH_2Cl$	CH_3MgI	$CH_3{-}CH{=}C(Cl){-}CH_2 + CH_3{-}CH(CH_3){-}C(Cl){=}CH_2$ 50 18	[143]
5	$CH_3CH{=}CH{-}CH_2Cl$	PhMgBr	$CH_3CH(Ph){-}CH{=}CH_2$ 59	[144]
6		PhMgBr	 55	[145]

4. The cleavage of compounds of different classes

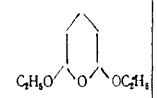
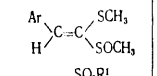
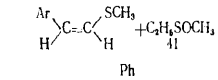
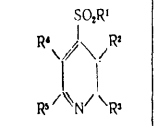
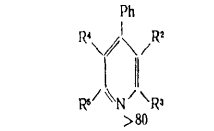
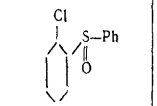
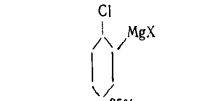
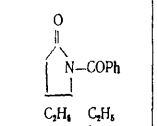
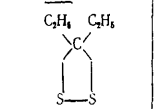
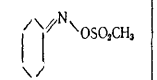
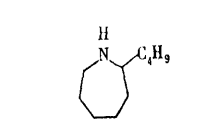
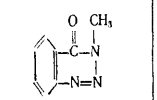
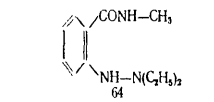
Isolated examples involving the heterolysis of a carbon–element σ-bond by organomagnesium compounds derived from organic compounds of different classes can be found in the literature. Examination of examples 1–7 (Table 9) shows that these are related reactions, since the yield of the products indicated in Table 9 depends on the solvating capacity of the solvent and also on the stability of the fragments of the molecules of the initial compound into which they can cleave heterolytically by RMgX at the carbon–element bond.

Examples 8–10 (Table 9) show that the heterolysis of the carbon–element σ-bond examined in the present review is a special aspect of a wide range of reactions involving the cleavage of element–element bonds by Grignard reagents.

IV. Conclusion

In conclusion of the review, it is essential to note that the heterolysis of a carbon–element σ-bond is hardly likely to be very important for organic synthesis, in the first place because well tried synthetic methods for the preparation of stable carbonium ions or carbanions already exist. Using the latter as the starting materials, it is possible to obtain fairly readily the required products without resorting to the cleavage by RMgX of substrates comprising the species under consideration [a carbonium ion (and its counterion) and the carbanion (and its counterion)].

Table 9. Yields of the products of the cleavage of different class of organic compounds.

No.	Substrate	Reagent	Yield of product, %	Refs.
1		PhMgBr	$Ph{-}CH(OC_2H_5){-}(CH_2)_3{-}CH(OH){-}Ph$ 100	[146]
2	$R{-}S{-}C{\equiv}N$	R^1MgX	$R{-}S{-}R^1$ >40	[147]
3		C_2H_5MgBr	 41	[148]
4		PhMgBr	 >80	[149]
5		PhMgBr	 85%	[150]
6	$(CH_3)_2N{-}CH(SCH_3)_2$	PhMgBr	$(CH_3)_2N{-}CH(Ph)_2$ 30	[151]
7		$n\text{-}C_6H_{13}MgBr$	$n\text{-}C_6H_{13}CO(CH_2)_3NH{-}COPh$	[152]
8		CH_3MgI	$(C_2H_5)_2C(CH_2SCH_3)SH$ 86	[153]
9		C_4H_9MgI	 57	[154]
10		C_2H_5MgI	 64	[155]

However, the possibility of the heterolysis of a carbon–element (element–element) σ-bond by organomagnesium compounds must always be taken into account for compounds which can fragment into stable charged species.[156–158]

Thus reactions in which carbon–element bonds are apparently cleaved have been described in the literature, although the authors of the communications quoted did not describe the identification of the following compounds [the products of the heterolytic reactions (8)–(10) respectively]:

$(C_2H_5)_2N—CH_2C\equiv C—CH_2—N(C_2H_5)_2$, $(CH_3)_2N—CH_2CH_3$, $PhCH(OCH_3)Ph$.

$$(C_2H_5)_2N—CH_2—C\equiv CMgI + ClSi(CH_3)_3 \rightarrow (C_2H_5)_2N—CH_2—C\equiv C—Si(CH_3)_3 \text{ (Ref.156).} \quad (8)$$

$$(CH_3)_2N—CH_2—CH(Ph)—CO—CH_3 + CH_3MgI \rightarrow \rightarrow (CH_3)_2N—CH_2CH(Ph)—C(CH_3)_2 \text{ (Ref.157)} \quad (9)$$
$$\quad\quad\quad

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Reactions of phosphorus(III) chlorides with carbonyl compounds

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ABSTRACT. The composition of the products of the interaction of phosphorus(III) chlorides with carbonyl compounds and the pathways leading to their formation are analysed as a function of the structure of the initial reactants and the experimental conditions. The catalytic role in the primary processes of the admixture of hydrogen chloride in phosphorus(III) chlorides is discussed. The influence of the functional group in substituted aldehydes and ketones and of the third reactant on the course of the reactions and on the nature of the final product is demonstrated.

The bibliography includes 231 references.

Contents

I. Introduction 251
II. Reactions of phosphorus(III) chlorides with carbonyl compounds in the absence of a third reactant 251
III. Reactions of phosphorus(III) chlorides with carbonyl compounds in the presence of a third reactant 259
IV. Conclusion 263

I. Introduction

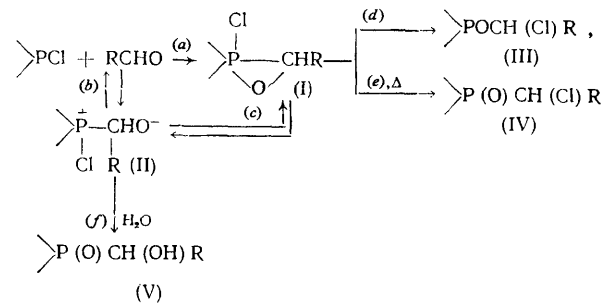
The reactions of phosphorus(III) chlorides with carbonyl compounds have already been discussed in reviews,[1,2] but the later of the two was published 20 years ago. Since then considerable advances have been made in the study of these reactions and a large amount of new scientific data, which have significantly altered many of our ideas about these reactions, has accumulated. The structure of the products of the interaction of phosphorus(III) chlorides with carbonyl compounds and the pathways leading to their formation depend very significantly on whether the reaction is carried out in the presence of a third reactant or in its absence. In the present review, attention is concentrated on the survey of literature data published during the last 20 years. The endeavour to demonstrate the evolution of views on the reactions considered led us to include in the review also certain studies from an early period.

II. Reactions of phosphorus(III) chlorides with carbonyl compounds in the absence of a third reactant

1. Aldehydes

More than 100 years ago, Fossek[3] established for the first time that phosphorus trichloride interacts vigorously with aldehydes to form thick oily adducts. Michaelis[4] attributed to them the structure of cylcophosphorane (I) (Scheme 1, pathway *a*), i.e. he postulated that the interaction proceeds with an increase in the coordination number of phosphorus. Conant[5] initially fully supported Michaelis's scheme but on the basis of kinetic studies he assumed the initial formation of a dipolar product (II) (pathway *b*)[6] capable of being converted into the phosphorane (I) (pathway *c*).

Scheme 1



Page,[7] Kabachnik,[1] and Atherton et al.[8] held a different view on the nature of the primary process. They assumed that phosphorus(III) chloride is an electrophile and that the coordination number of the phosphorus atom does not change in the primary process.

$$\text{PCl} + \text{RCHO} \rightarrow \underset{\text{(III)}}{\text{POCH (Cl) R}}.$$

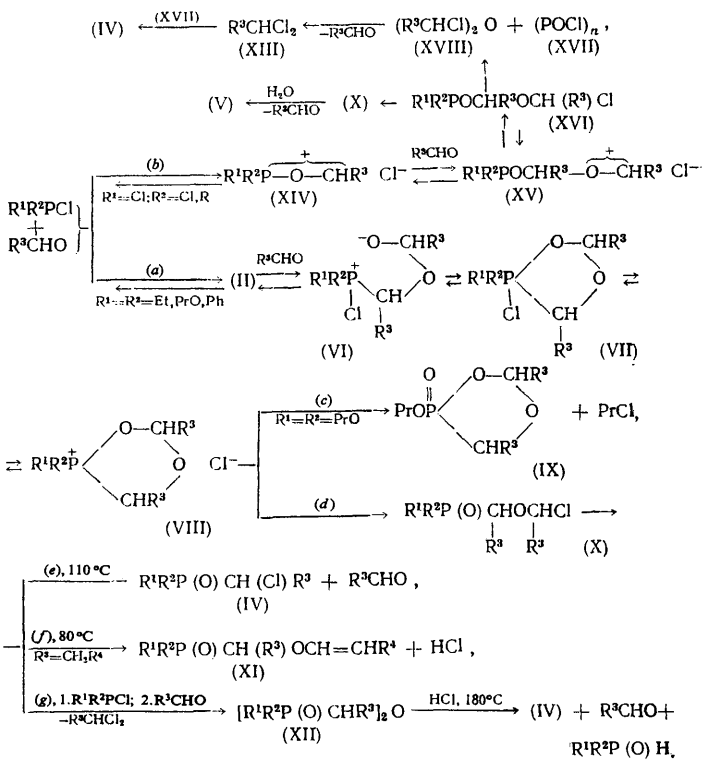
Pudovik and Khairullin[2] maintained the view that phosphorus(III) chlorides behave as nucleophiles in the primary step of the interaction and, taking into account new data,[1,7,8] supplemented the Michaelis–Conant mechanism by introducing into it the new pathways *d* and *e*. If the product of the direct interaction of phosphorus(III) chloride with an aldehyde is pyrolysed (pathway *e*) or is treated with water (pathway *f*), then stable α-chloroalkyl derivatives [compounds (IV)] and α-hydroxyalkyl derivatives [compounds (V)] of phosphorus(IV) are formed.[1,2,9–15]

On the basis of the structures of compounds (IV) and (V), the investigators assumed that only one aldehyde molecule is consumed in the formation of the product in the reaction of phosphorus(III)

chloride with aldehydes. However, since the 1970's, studies have been published indicating the consumption of two aldehyde molecules per P–Cl bond.[16–21] From the character of the effect of the nature of the substituents in phosphorus(III) chlorides and aldehydes on the rate of reaction, it was concluded that PCl_3 and $RPCl_2$ exhibit electrophilic[16–19,22–24] reactivity, while R^1R^2PCl and $(R^1O)(R^2O)PCl$ exhibit nucleophilic activity.[16,17,20] Thus the interaction of secondary chlorophosphines with benzaldehydes affords the salts (VIII), which are then converted via the Arbuzov reaction into compounds (X) (Scheme 2, pathways *a* and *d*),[24] while the interaction of chlorodiphenylphosphine with aliphatic polyfluoroaldehydes gives rise to the stable phosphoranes (VII).[20] The phosphorane (VII) with $R^1 = R^2 = PrO$ is stabilised as a result of the elimination of propyl chloride with retention of the 1,4,2-dioxaphospholan ring (IX) (pathways *a* and *c*). The formation of compounds (VII) and (VIII) can probably be represented in the following way: as a result of the nucleophilic attack by the lone pair of phosphorus(III) on the carbon atom of the carbonyl group, the dipolar ion (II) is formed and combines with a second aldehyde molecule, being converted into a new dipolar ion (VI). The latter is sterically more favourable for the formation of the phosphorane structure (VII) compared with the ion (II).

At 80 °C, compound (X) is dehydrochlorinated to the product (XI) (pathway *f*),[18] while at 110 °C it splits off an aldehyde molecule and is converted into the familiar compound (IV) (pathway *e*).[23] The phosphine oxide (X) also readily reacts with chlorodiphenylphosphine and an aldehyde, affording the alkylidine chloride (XIII) and the ether (XII) (pathway *g*). The pyrolysis of the latter in the presence of HCl leads, as in the case of the product (X), to compound (IV).[16]

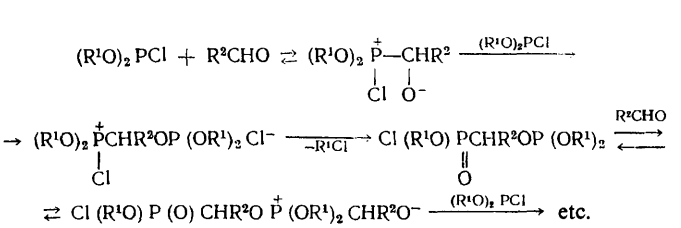
Scheme 2



In the case of phosphorus(III) chlorides exhibiting electrophilic properties, the primary products apparently arise from the exchange of chlorine atoms at the phosphorus(III) for a new group[16] and are formed as a result of the nucleophilic attack by the oxygen atom of the carbonyl group on the phosphorus(III) atom, which leads to the ion pair (XIV) (pathway *b*). The cation (XIV), whose stability is enhanced by the delocalisation of the charge, combines with the next aldehyde molecule, affording the new ion pair (XV). Compounds (XV) and (XVI) are converted into the product (X) via a stage involving the formation of a quasi-phosphonium salt of type (VIII). Compound (X) readily gives rise to the α-hydroxyalkyl derivative (V) of phosphorus(IV) on treatment with water and can also react chemically via pathways *e* and *f*.[18]

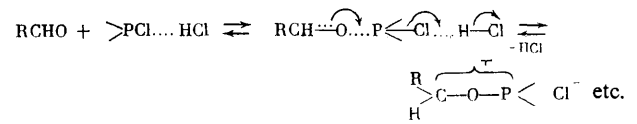
In later studies,[22,23] the isolation of compounds (XIII) and (XVIII) after the reaction of PCl_3 with benzaldehyde led to the hypothesis that the phosphorus-containing product (XVII) is formed and reacts with benzylidene chloride (XIII) via the mechanism of the Arbuzov reaction. The structure of compound (XVII) was not demonstrated rigorously and it is also difficult to postulate the interaction of a compound having a P(III)–Cl bond with a weak electrophile such as benzylidene chloride. It has still not been elucidated from what intermediate are the ethers (XVIII) formed directly under mild conditions. However, it is entirely possible that it is a compound containing one or several 1-(1′-chloroalkoxy)-alkoxy-groups at the phosphorus atom. One should also note that, in the interaction of formaldehyde (paraformaldehyde) with phosphorus(III) chloride, the formation of organophosphorus compounds with $POCH_2OCH_2Cl$ and $P(O)CH_2OCH_2Cl$ structural fragments has not so far been confirmed experimentally, although the detection or isolation of the ether (XVIII, $R^3 = H$) after this reaction has been frequently reported.[9,25–27]

The manifestation by dialkyl phosphorochloridites of both nucleophilic and electrophilic properties at different stages of the reaction with aldehydes has been assumed in some investigations:[27,28]

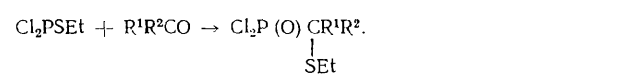


The demonstration of the catalytic effect of the HCl impurity in phosphorus(III) chlorides on the course of the reactions considered is extremely important.[29,30] It was found that phosphorus(III) chloride freed from the HCl impurity by treatment with alkyl vinyl ethers (AVE) does not interact with an aldehyde at 20 °C. The process begins only after the introduction of HCl into the reaction mixture. The catalytic effect of the HCl impurity had been detected previously in the reaction of phosphorus(III) chlorides with alkene oxides,[31,32] carboxylic acids,[33] and acetals.[34,35] The catalytic role of the HCl impurity in phosphorus(III) chlorides in exchange reactions is also emphasised in a recent review.[36] The catalytic role of HCl in the interaction of aldehydes with phosphorus(III) chlorides can be

reflected by a mechanism analogous to that of the reactions of the latter with alkene oxides and acetals:

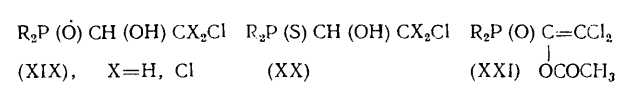


The nature of the phosphorus(III) chloride can alter radically the mode of its interaction with carbonyl compounds. It has been shown recently that ethyl phosphorodichloridothioate reacts with benzaldehyde and acetone via the P–S bond and not with participation of the P–Cl bond.[37,38]



The interaction of phosphorus(III) chlorides with aldehydes containing functional groups as substituents has also been investigated. Thus mercurated acetaldehyde reacts with phosphorus(III) chlorides to form *O*-derivatives, i.e. the reaction takes place with transfer of the reaction centre.[39]

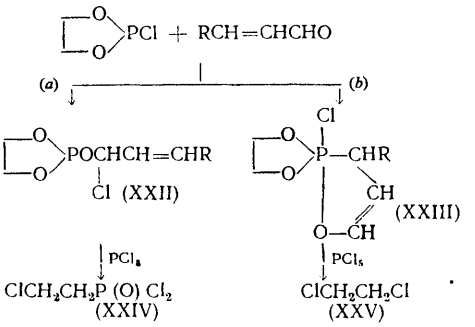
It has been suggested that secondary chlorophosphines exhibit nucleophilic reactivity in their reactions with α-chloroaldehydes and that an adduct having the betaine structure (II) is formed.[2,40,41] In order to obtain the individual compounds (XIX)–(XXI), the R_2PCl + $X_2ClCCHO$ reaction mixture is treated with proton-donating compounds or acetic anhydride.



However, one should note that the possibility of the initial interaction of various secondary chlorophosphines with chloroaldehydes has not been confirmed experimentally, while the products (XIX)–(XXI) can be formed as a result of the initial hydrolysis of the chlorophosphines to the corresponding acid and the addition of the latter to the carbonyl group of the aldehyde. A structure analogous to that that of compound (III) has been attributed[42] to the product of the interaction of chloral with 2-chloro-1,3,2-dioxaphospholan, but adequate evidence for this has not been adduced.

2-Chloro-1,3,2-dioxaphospholan reacts vigorously with acroleine and crotonaldehyde to form oligomers (Scheme 3).[43] On the basis of the structure of the products (XXIV) and (XXV) obtained after treating the oligomers with phosphorus pentachloride, the authors concluded that the 1,2-addition of the chloride to the carbonyl group with dissociation of a P–Cl bond mainly takes place, i.e. a chlorine atom at the phosphorus(III) atom is exchanged for a new group [pathway *a*, compound (XXII)]. The partial 1,4-addition of the phosphorus atom to the conjugated system without the rupture of a P–Cl bond and with increase in the coordination number of phosphorus from 3 to 5 has also been postulated [pathway *b*, compound (XXIII)].

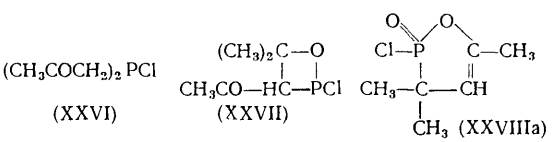
Scheme 3



It seems to us that the interaction of phosphorus(III) chlorides with unsaturated aldehydes has still been studied inadequately and that more far reaching studies are necessary to establish the real reaction mechanism.

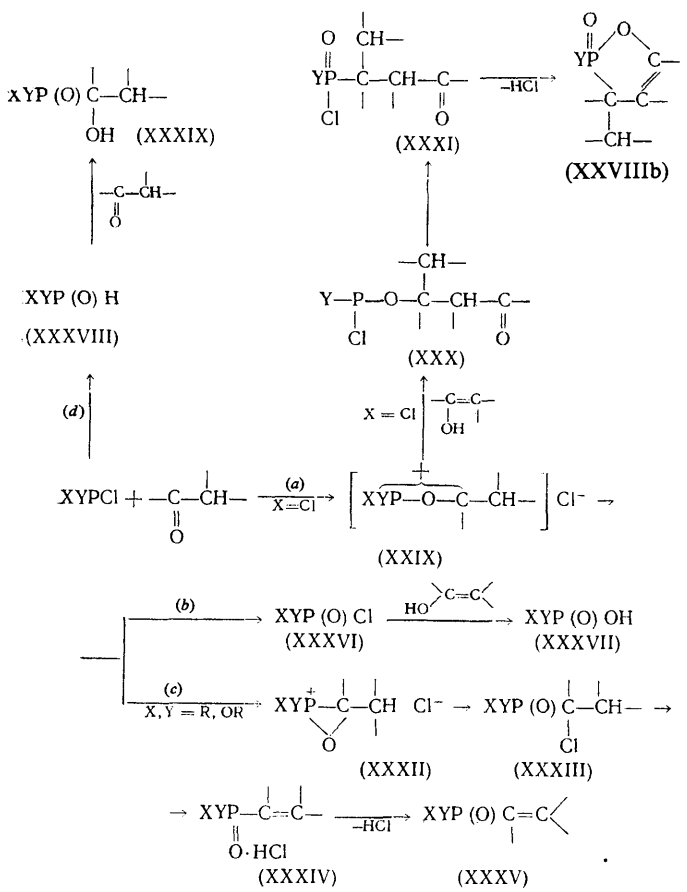
2. Ketones

In the past century, Michaelis[1,2] already established that in the presence of aluminium trichloride PCl_3 and $RPCl_2$ condense with acetone in proportions of 1 : 2. The acyclic structure (XXVI) was attributed initially to the reaction product, which has come to be called "the Michaelis chloride" in the literature. Later the cyclic structure (XXVII) was assigned to it. Much later, in the study of the reactions of phosphorus(III) chlorides with unsaturated ketones, it was possible to show that the product has the structure of 2-chloro-2-oxo-1,2-oxaphospholene (XXVIIIa).[44]



During the last 15 years, it has been found that aliphatic and aliphatic-aromatic ketones react with phosphorus(III) chlorides also in the absence of $AlCl_3$ but on heating. The products of the reactions of PCl_3 and phosphorus(III) dichlorides are derivatives of 1,2-oxaphospholene (XXVIIIb) (Scheme 4, pathway *a*).[13,45–50]

Scheme 4

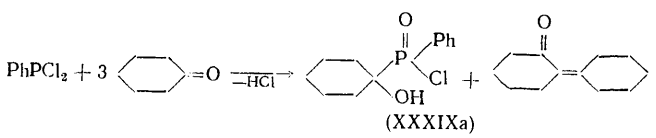


The authors suggest that the primary process is the exchange of a chlorine atom at the electrophilic phosphorus(III) atom (Scheme 4, pathway *a*). The ion pair (XXIX) reacts with the enolic form of the ketone, affording a γ-ketoester chloride of phosphorus or phosphonous acid (XXX), which isomerises to the phosphorus(IV) derivative (XXXI) capable of cyclisation, with elimination of HCl, to the final product (XXVIIIb). If cyclohexanone is used as the ketone, then a polycyclic compound is formed and this too is a substituted 1,2-oxaphospholene.[51]

The formation of the intermediate compound (XXXI) was confirmed by IR spectroscopy and NMR. In the studies indicated, the question of the pathways leading to the transition (XXX) → (XXXI) was not discussed. It is entirely possible that compound (III) decomposes into partial phosphorus acid chloride and an unsaturated ketone, which interact, affording the product (XXXI). HCl probably favours such decomposition.

Chlorodiethyl- and chloroethylphenyl-phosphines and phosphorochlorodites react with ketones,[50–53] including cyclic ketones,[53–56] in proportions of 1:1 to form α-chloroalkyl derivatives of phosphorus(IV) (XXXIII) (Scheme 4, pathways *a* and *c*), which split off HCl on heating or on treatment with a base and are converted into the unsaturated compounds (XXXIV) and (XXXV). It has been noted[53–57] that, in the interaction of secondary chlorophosphines with cyclohexanone, it was possible to detect by NMR the intermediate (XXXII) and to convert it into the more stable tetraphenylborate derivative. In the case of secondary chlorophosphines, the initial nucleophilic attack by the oxygen atom of the carbonyl group on the phosphorus(III) atoms has also been postulated. This entails the formation of the exchange product (XXIX), which is rapidly converted into compound (XXXII). However, one should note that, as for the reactions with aldehydes, there is a possibility that the secondary chlorophosphines may manifest nucleophilic properties, i.e. compound (XXXII) may be formed from the dipolar ion (II).

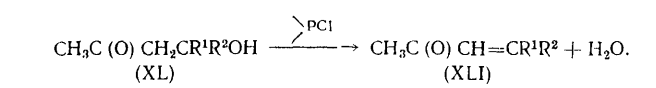
In contrast to other phosphorus(III) chlorides, chlorodiphenylphosphine reacts with acetone via pathway *b* (Scheme 4). When acted upon by the enolic form of the ketone, the acid chloride (XXXVI) is converted into the acid (XXXVII).[57] It reacts with cyclohexanone in an even more complex manner—via the three pathways *b*, *c*, and *d*—and compounds (XXXIII), (XXXVII), and (XXXIX) are isolated from the reaction mixture. The interaction of dichlorophenylphosphine with cyclohexanone also proceeds via pathway *d*. In this reaction, the initial reactants are consumed in proportions of 1:3.[58]



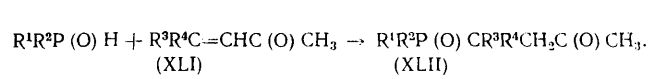
The reactions of cyclopentanone with dichlorophosphines and of cyclohexanone with phenyl phosphorodichloridite and dichloro-*p*-fluorophenylphosphine proceed via pathway *c* and the reaction products are cyclopentenyl and cyclohexenyl derivatives of phosphorus(IV) (XXXV).[13,59,60]

The reactions of phosphorus(III) chlorides with ketones having a second functional group have also been studied. For example, they interact in a fairly complex way with the hydroxyketones (XL). The structure of the final reaction product depends significantly both on the experimental conditions and on the nature of the substituents in the initial reactants. Whether or not triethylamine is present in the reaction mixture is an important factor.

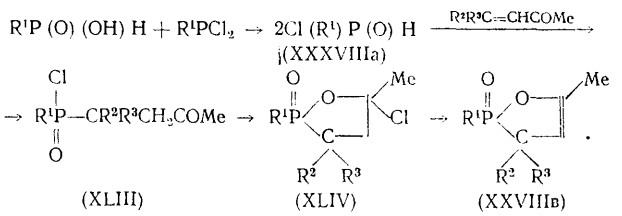
In the absence of a base, all the phosphorus(III) chlorides induce the rapid catalytic decomposition of β-ketoalcohols into αβ-unsaturated ketones (XLI) and water.[61–69]



Further reactions, leading to the final products, are therefore treated within the framework of reactions of unsaturated ketones with phosphorus(III) chlorides in the presence of water. The latter hydrolyses the phosphorus(III) chlorides to the corresponding acids XYPHO (XXXVIII) (X = Y = R, RO, Ar; X = OH, Y = R, RO, Ar; X = Y = OH). Acetic acid acts similarly on phosphorus(III) chlorides,[69,70] but the process is reversible. The acids (XXXVIII) exhibit different reactivities in relation to ketones (XLI); phosphinous acids add to the double bond, forming tertiary phosphine oxides (XLII), while the remaining acids are fairly inert under the conditions of the reaction considered.



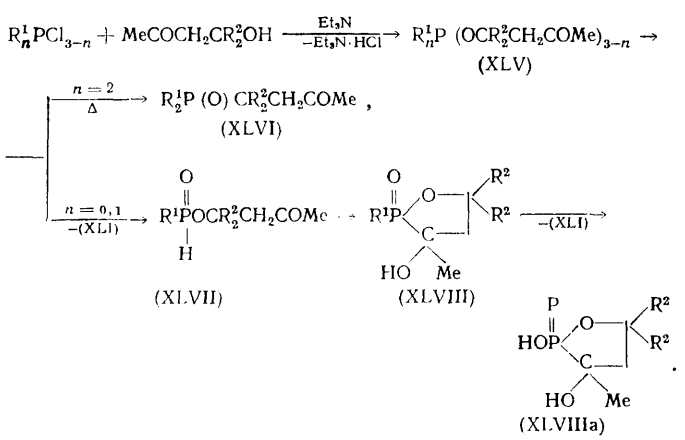
Dialkylphosphorous acids can be isolated in a pure form. Alkylphosphorous, phosphonous, and phosphorous acids react readily with phosphorus(III) chlorides, forming chemically extremely reactive partial acid chlorides (XXXVIIIa). The interaction of the latter with ketones (XLI) leads to Δ^4-1,2-oxaphospholenes (XXVIIIc). The formation of the intermediates (XLIII) and (XLIV) was demonstrated not only by spectroscopic methods but also by isolating them, for certain substituents R^1, R^2, and R^3, in a pure form. The claim that the 1,2-oxaphospholene systems are formed as a result of intermolecular and intramolecular nucleophilic substitution at the phosphorus(III) atom[71] in the reactions considered is controversial.



(XLIII) (XLIV) (XXVIIIв)

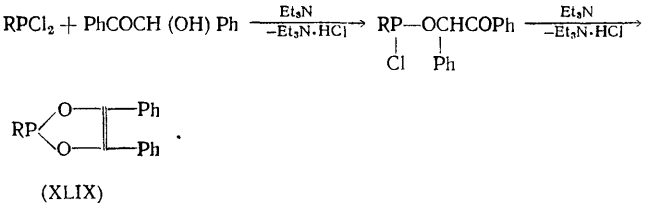
Without exaggeration, one can now claim that the idea of the chemists of the Kazan School that β-ketoalcohols undergo catalytic decomposition to an unsaturated ketone and water and that the phosphorus(III) chloride interacts initially with water and not with the carbonyl compounds, as well as the idea that the partial acid chlorides (XXXVIIIa) are formed as intermediates were fully confirmed in subsequent studies[70] and constitute a major contribution to the theory of the reactions of phosphorus(III) chlorides with all aldehydes and ketones in the presence of proton-donating compounds, whose investigation was initiated more than a century ago.

In the presence of triethylamine, the character of the reaction of phosphorus(III) chlorides with hydroxyketones is completely different: the primary process involves the hydroxy-group without altering the coordination number of the phosphorus atom.[69,72–78] If the exchange products (XLV) contain only one γ-ketoalkoxy-group, then on heating they rearrange to the phosphorus(IV) derivatives (XLVI);[73,77] if there are two such groups, then an unsaturated ketone is split off and the acid (XLVII) cyclises to the oxaphospholan (XLVIII).[69,72–76,79] If there are three such groups, then yet another ketone (XLI) molecule is eliminated[69] and the oxaphospholanol (XLVIIIa) is formed:



(XLVII) (XLVIII) (XLVIIIa)

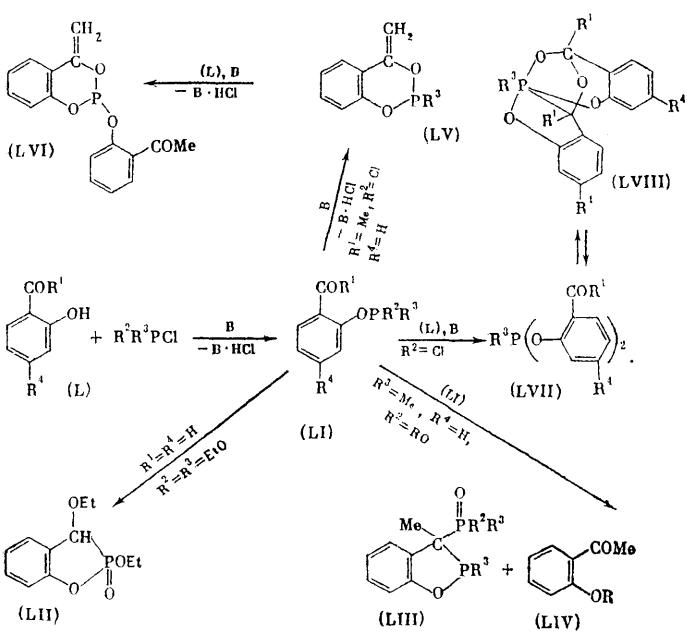
The products of the reactions of benzoin with phosphorus(III) di- and tri-chlorides are unsaturated phosphorus(III) derivatives (XLIX) formed as a result of the primary exchange and subsequent cyclisation.[80,81]



(XLIX)

Phosphorus(III) chlorides interact in a very complex manner with *o*-carbonylphenols (L). The subsequent reactions of the primary products (LI) depend on the nature of the groups R^1, R^2, R^3, and R^4 and the experimental conditions. The products are the most stable in the case of phosphorus(III) monochlorides.[82,83] However, when R^1 = H, heterocyclisation proceeds readily as a result of the attack by the lone pair the phosphorus(III) atom on the carbon atom of the carbonyl group and compound (LII) is formed (Scheme 5).[84]

Scheme 5



Compounds (LIII) and (LIV) are the products of the slow interaction of two (LI, R^1 = Me) molecules. In the presence of a base (B), compound (LI, R^2 = Cl) is converted into the products (LV) and (LVII) as a result of intramolecular (R^3 = RO, Cl)[82,83,85] or intermolecular (R^3 = alkyl, aryl)[82,85–88] nucleophilic substitution. When R^3 = Cl, the product (LV) can enter into an exchange reaction with formation of compound (LVI).[85] Compounds (LVII)

are entirely stable if R^4 is the sterically bulky 2,4,5,6-tetramethylphenyl group or if the electrophilicity of the carbonyl group is reduced (R^1 = OMe).[86] In the absence of these factors, compounds (LVII) are converted into the cyclic phosphoranes (LVIII) as a result of oxidative cyclisation.[85–88] When R^1 = 2,4-$Me_2C_6H_3$ and R^4 = OMe, the phosphorane (LVIII) is in equilibrium with the phosphonous form.[86]

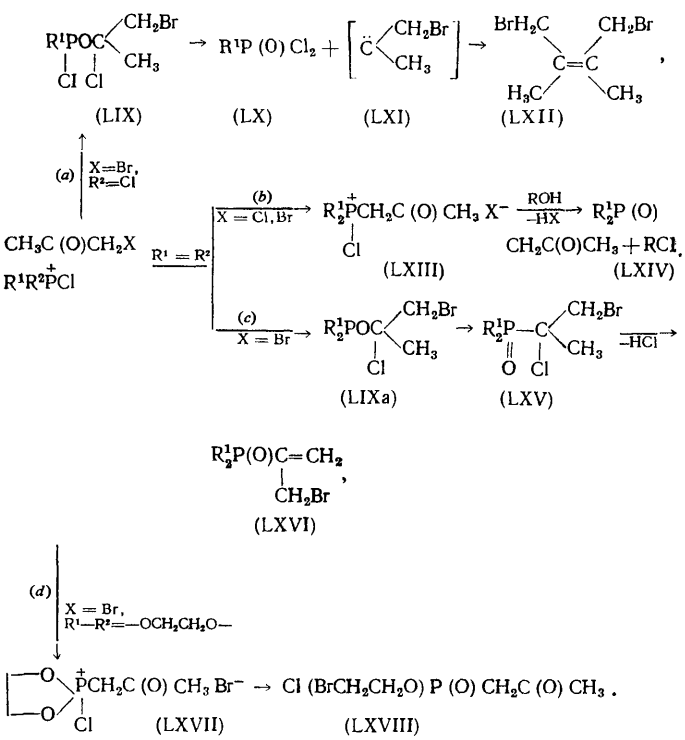
The interaction of salicylaldehyde with PCl_3 under severe conditions (high temperatures) leads to 2,3-dichloro-2-oxo-4,5-benzo-1,2-oxaphospholan.[89,90]

Metal derivatives of ketones react readily with phosphorus(III) chlorides. Thus the latter react with α-mercurated ketones with transfer of the reaction centre and the formation of unsaturated esters.[91]

The influence of the nature of the substituents at the phosphorus(III) on the mode of interaction can be traced in relation to the reactions of phosphorus(III) chlorides with trialkylstannylacetone:[91] PCl_3 and the secondary chlorophosphines react without transfer of the reaction centre, phosphorochloridites and phosphorodichloridites react with transfer of the reaction centre, while phosphonous ester chlorides afford a mixture of *O*- and *C*-phosphorylated products.

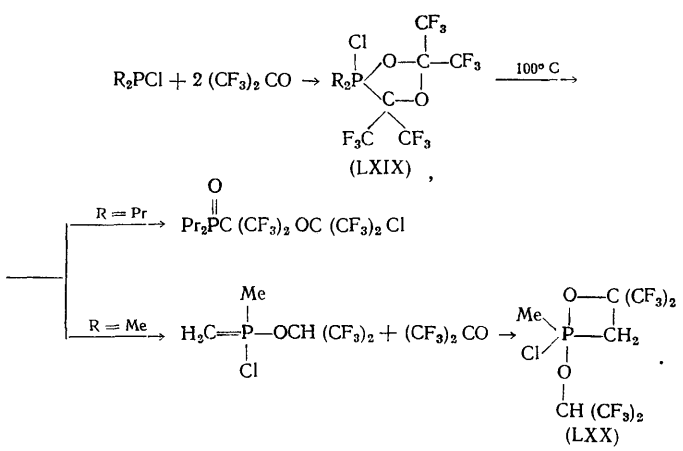
Depending on the nature of the substituents at the phosphorus(III) atom, phosphorus(III) chlorides can interact with α-monohalogenoketones both at the α-carbon atom and at the carbonyl group.[92–95] The reaction of phosphorus(III) dichlorides with bromoacetone results in the formation of phosphorus(IV) dichlorides (LX) and the dibromoalkene (LXII) (Scheme 6).[92] It has been suggested that phosphorus(III) dichlorides exhibit electrophilic properties and that initially a chlorine atom at the phosphorus(III) atom is substituted by a new group [pathway *a*, compound (LIX)]. Compound (LIX) then decomposes at the C–O bond with formation of the dichloride (LX) and the carbene (LXI), which dimerises to the alkene (LXII). Secondary chlorophosphines react with α-halogenoketones via two pathways:[93–95] in the first pathway, phosphorus(III) combines with halogenoacetone (nucleophilic properties) to form the phosphonium salt (LXIII), which can be isolated in a pure form[94] or can be converted into the phosphine oxide (LXIV) on treatment with alcohols,[93,95] water, or acetaldehyde[95] (pathway *b*); in the other pathway, a chlorine atom at the phosphorus(III) atom is substituted by a new group (electrophilic properties) with formation of the intermediate (LIXa), which subsequently isomerises to the phosphorus(IV) derivative (LXV); the latter is dehydrochlorinated, affording the product (LXVI) (Scheme 6, pathway *c*). 2-Chloro-1,3,2-dioxaphospholan (R^1–R^2 = $-OCH_2CH_2O-$) exhibits nucleophilic properties, combining with bromoacetone and affording the quasi-phosphonium salt (LXVII), which is converted into the product (LXVIII) via the Arbuzov reaction.[93]

Scheme 6

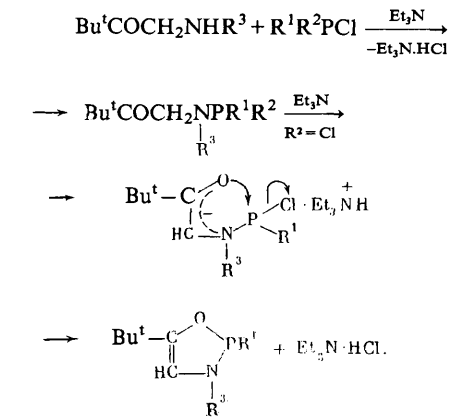


Hexafluoroacetone reacts with secondary chlorophosphines similarly to polyfluoroaldehydes[20] in proportions of 2:1 to form the phosphorane (LXIX) with the 1,2,4-dioxaphospholan ring.[96–98]

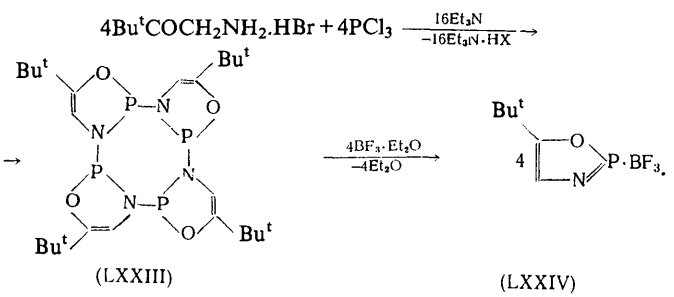
Compound (LXIX, R = Pr) undergoes the Arbuzov reaction[96] at 100 °C, while the corresponding compound with R = Me is converted into the cyclic compound (LXX). It is suggested that the reaction proceeds via the intermediate formation of an ylide.[98]



α-(*N*-Alkyl)aminoketones interact with phosphorus(III) chlorides with dissociation of an N–H bond. When there is a chlorine atom at the phosphorus(III) atom, the exchange products (LXXI) readily undergo intermolecular cyclisation to the product (LXXII).[99–104]

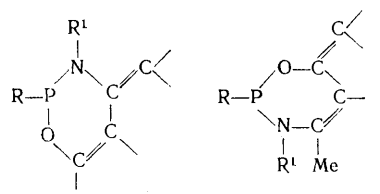


The salt of the unsubstituted aminoketone reacts with PCl_3 to produce the complex polycyclic compound (LXXIII) which is converted into a product with a two-coordinated phosphorus atom (LXXIV) on treatment with boron trifluoride etherate. Compound (LXXIV) was identified as a complex with BF_3.[105]



(LXXIII) (LXXIV)

The reactions of phosphorus(III) dichlorides with *N*-monosubstituted enaminoketones lead to 1,3,2-oxazaphosphorinanes with a diene system of C=C bonds [compounds (LXXV)], their exocyclic C=C bond adjoining the nitrogen atom.[106] Their product with the exocyclic C=C bond at the oxygen atom [compound (LXXVI)] has not been detected.

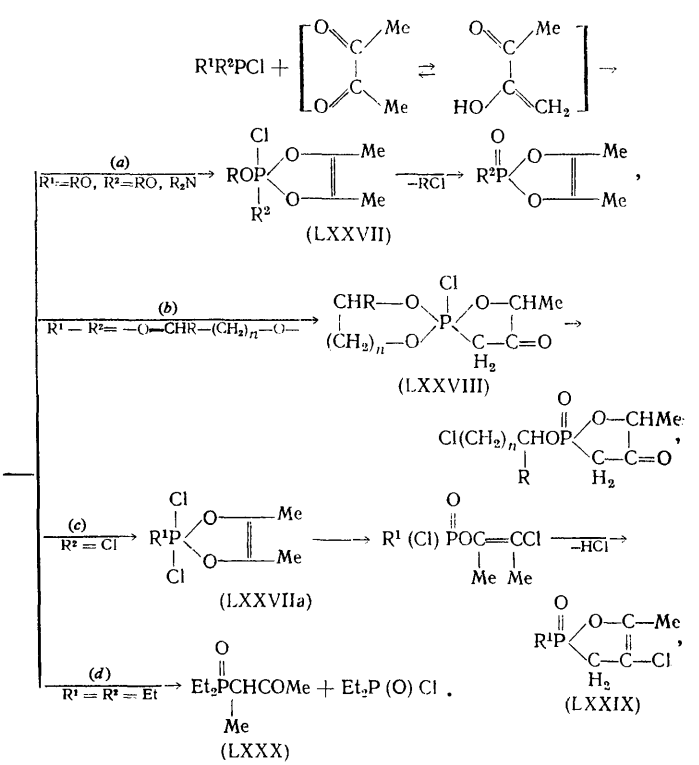


(LXXV) (LXXVI)

Although phosphorus(III) chlorides react with saturated aminoketones[99–104] and the nitrogen analogues of acetylacetone and acetoacetic ester[107] exclusively at the nitrogen atom, the conclusion that the enaminoketones are initially phosphorylated at the O or N atom must be reached with much caution, since there is a possibility of prototropic interactions between the primary exchange products and also compounds (LXXV) and (LXXVI).

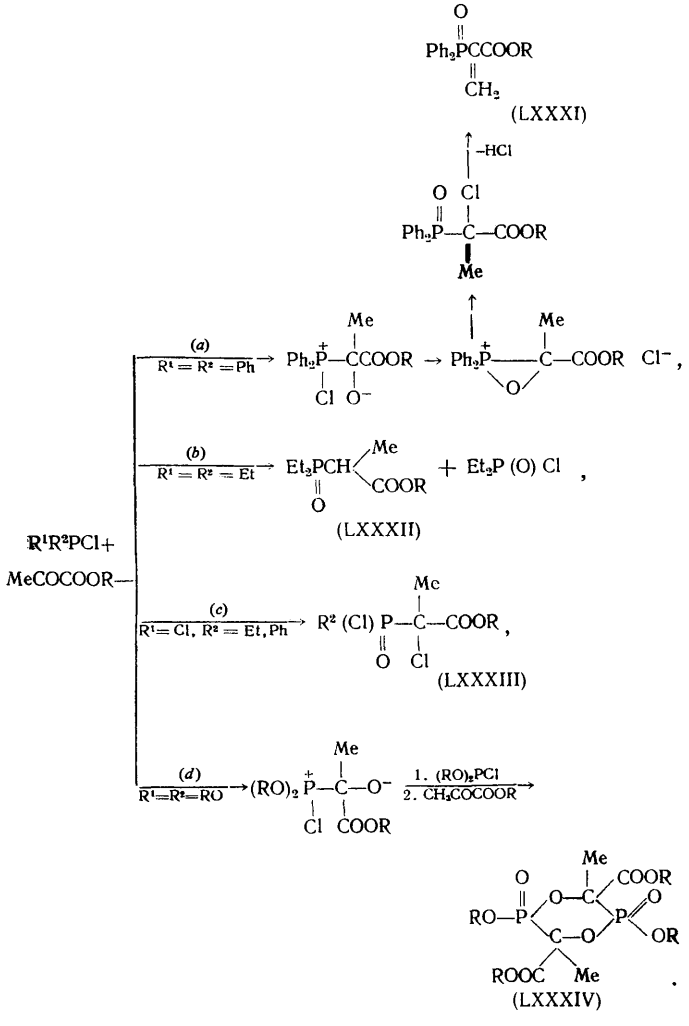
The reactions of phosphorus(III) chlorides with α- and β-dicarbonyl compounds (diacetyl, acetylacetone, and pyruvic and acetoacetic esters) have been investigated. Diacetyl reacts exothermically with all phosphorus(III) chlorides. The structure of the reaction product depends on the nature of the substituents at the phosphorus(III) atoms. It is believed that acyclic phosphoromonochloridites react with the ketone form of diacetyl (Scheme 7, pathway *a*),[108–111] while cyclic phosphorochloridites react with the enolic form (Scheme 7, pathway *b*).[112] The adducts (XXVII) and (XXVIII) are converted into phosphorus(IV) derivatives via the mechanism of the second stage of the Arbuzov reaction. The formation of the phosphorane (XXVII) has been confirmed by ^{31}P NMR.[111] The adduct (XXVIIa) formed in the first stage of the reactions of dichlorophosphines is subsequently converted into the 1,2-oxaphospholene (XXIX), i.e. the reaction proceeds with formation of a new P–C bond (Scheme 7, pathway *c*).[113,114] The reaction of chlorodiethylphosphine with diacetyl produced the tertiary phosphine oxide (XXX) and the chloride of diethylphosphinic acid (Scheme 7, pathway *d*).[115] The authors assumed the possibility of the involvement in the reaction of the enolic form of diacetyl and the formation of diethylphosphinous acid as an intermediate. Although it follows from mechanisms *a*, *b*, and *c* that the phosphorus atom exhibits biphilic properties, there is no unanimous view in the literature about the character of the primary step of the interaction. Whereas the role of phosphoromonochloridites in the primary step of the reaction remains unelucidated,[108–111] the role of nucleophiles is attributed to the more electrophilic primary dichlorophosphines.[113,114] At the same time, the possibility of a donor–acceptor interaction of the oxygen atom of diacetyl with the phosphorus(III) atom of chlorodiethylphosphine[115] (electrophilic properties)—the most nucleophilic of phosphorus(III) chlorides—has been postulated. It follows from the data presented that the role of the phosphorus(III) chloride in the primary step of the interaction has not been clearly defined and that additional studies are necessary in order to throw light on this problem.

Scheme 7



According to literature data, pyruvate esters react, in contrast to diacetyl, with phosphorus(III) chlorides exclusively in the ketone form and the structure of the reaction products depends significantly on the nature of the substituents at the phosphorus(III) atom. Thus the product of the reaction of chlorodiphenylphosphine (Scheme 8, pathway *a*) is the unsaturated phosphine oxide (LXXXI),[116] while the product of the reaction of chlorodiethylphosphine (Scheme 8, pathway *b*) is the unsaturated phosphine oxide (LXXXII).[115–117]

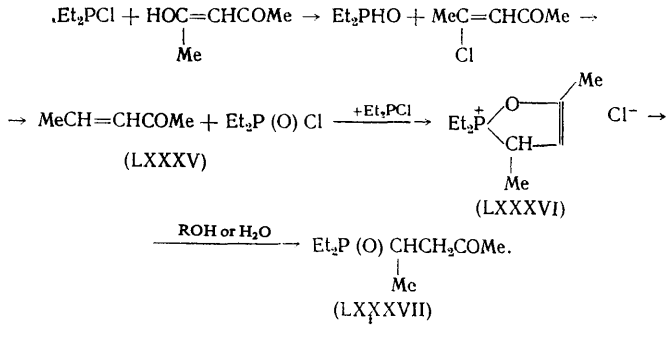
Scheme 8



The reaction of pyruvate esters with primary dichlorophosphines (Scheme 8, pathway *c*) gives rise to the chlorides of phosphinic acids (LXXXIII) with functional-group substituents,[116,118] while their reaction with dialkyl phosphorochloridites (Scheme 8, pathway *d*) affords 2,5-dialkoxy-3,6-dialkoxy-carbonyl-3,6-dimethyl-2,5-dioxo-1,4-dioxa-2,5-diphosphorinanes (LXXXIV).[119]

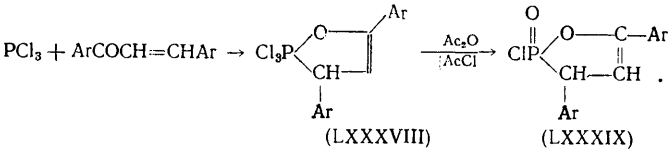
It is believed that in the reactions described, chlorodiphenylphosphine exhibits nucleophilic reactivity,[116] while dialkyl phosphorochloridites exhibit nucleophilic reactivity in the first stage and electrophilic reactivity in the second.[119]

The interaction of chlorodiethylphosphine with acetylacetone in the absence of a base is completed by the formation of the chloride of diethylphosphinic acid and the phosphonium salt (LXXXVI), which is converted into the tertiary phosphine oxide (LXXVII) on treatment with alcohols or water.[57,115] The authors believe that the reaction proceeds with participation of the enolic form of the β-diketone via the intermediate formation of diethylphosphinous acid and the unsaturated ketone (LXXXV). The product of the reaction of the latter with the initial phosphine is the salt (LXXXVI).



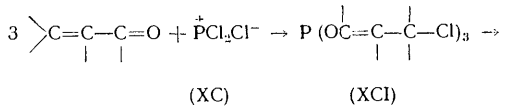
A similar scheme has been postulated also for the reaction of chlorodiethylphosphine with acetoacetic ester.[115]

The study of the reactions of phosphorus(III) chlorides with ketones containing an alkylidene group as a second substituent was initiated by Conant as early as 1917.[1,2] He suggested that the reaction proceeds via the 1,4-addition of phosphorus(III) to the ends of the conjugated system with formation of the phosphorane (LXXXVIII),[120] which is converted into the oxaphospholene derivative of phosphorus(IV) (LXXXIX) on treatment with acetic anhydride.

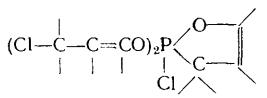


Later Drake and marvel[44] established that the 1,4-addition of PCl_3 to alkyl- and aryl-substituted unsaturated ketones is a general feature although in the study of more complex systems such universality was questioned.[121,122]

In view of the difficulty of alkylating PCl_3 and the results of his own studies of the interaction of this chloride with five- and six-membered cyclic unsaturated ketones, Kabachnik[1] criticised the 1,4-addition mechanism proposed by Conant. He suggested instead a mechanism involving the 1,4-addition of the charged $P^+Cl_2Cl^-$ fragments to the ends of the conjugated system of the ketone, which results in the formation of the γ-chlorinated unsaturated phosphite ester (XCI). The latter is converted via the mechanism of the first stage of the Arbuzov reaction into compound (XCII) with the 1,2-oxaphospholene ring.



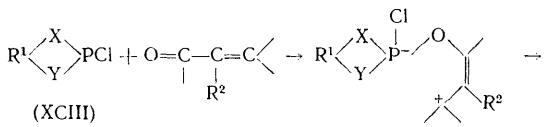
(XC) (XCI)



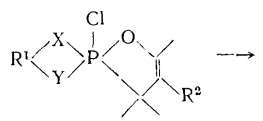
(XCII)

Thus, as for unsubstituted aldehydes, the nucleophilic substitution of a chlorine atom at the electrophilic phosphorus(III) by a new group is postulated. The interaction of PCl_3 with complex ketones such as 4-cholest-3-ynone and 10-methyl-2-oxo-$\Delta^{1,9}$-octalin has been interpreted similarly.[123] However, the manifestation of biphilic properties by phosphorus(III) and its 1,4-addition to the end of the conjugated system of the unsaturated ketones are generally acknowledged.[2,43,124–129]

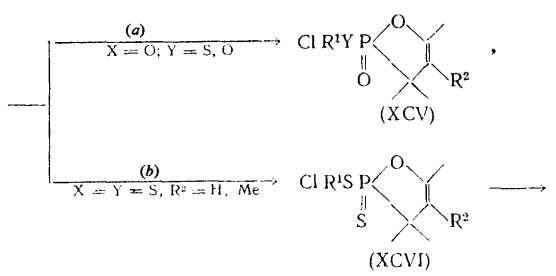
The reactions of unsaturated ketones with cyclic phosphorus(III) halides (XCIII) have been studied in detail. It has been suggested that cyclic phosphorus(III) chloride exhibit electrophilic reactivity in the primary step of the interaction.[128]



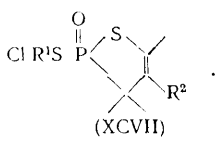
(XCIII)



(XCIV)



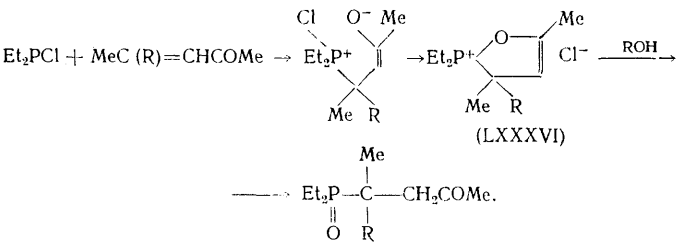
(XCV) (XCVI)



(XCVII)

The 1,4-adduct (XCIV) is stable when R^1 = arylene,[128] whereas in the case where R^1 = alkylene the adduct (XCIV) is converted into compounds (XCV) and (XCVI) via the mechanism of the second stage of the Arbuzov reaction.[2,43,124,125] When R^2 = H, compound (XCVI) isomerises to compound (XCVII) via Pishchimuka's mechanism.[126]

Important results were obtained in a study of the interaction of chlorodiethylphosphine with unsaturated ketones.[57] In this case, the 1,4-adduct was isolated in a pure form and some of its reactions were investigated. On the basis of the chemical shift of the phosphorus atom (126–128 p.p.m.), the structure of the quasi-phosphonium salt (LXXXVI) was attributed to it. Furthermore, chlorodiethylphosphine proved to be more reactive than phosphorus trichloride and phosphorus(III) dichlorides, whence it it possible to conclude that it manifests nucleophilic properties in the primary step of the interaction.

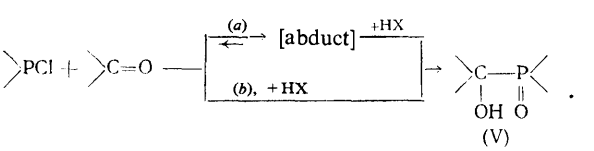


(LXXXVI)

The data described above show that during the last 15–20 years important information has been obtained about the reactions of phosphorus(III) chlorides with carbonyl compounds in the absence of a third reactant: the involvement in the role of the catalyst of the HCl impurity in the phosphorus(III) chloride and the consumption of two aldehyde molecules, in some cases also ketone molecules, for each P–Cl bond were established and new pathways in the reactions of ketones were discovered.

III. The reactions of phosphorus(III) chlorides with carbonyl compounds in the presence of a third reactant

The reactions of phosphorus(III) chlorides with carbonyl compounds in the presence of hydrolysing agents (water, acetic acid, and acetic anhydride with subsequent treatment of the reaction mixture with water) leads to 1-hydroxyalkylphosphonic and 1-hydroxyalkylphosphinic acid (V).[1,2] Under these conditions, it is possible to obtain initially the product of the addition of the phosphorus(III) chloride to the carbonyl compound and it can then be treated by the hydrolysing agent[6,130–132] (pathway *a*) or the initial reactants can be mixed in the presence of water, acetic acid, or acetic anhydride[132] (pathway *b*).

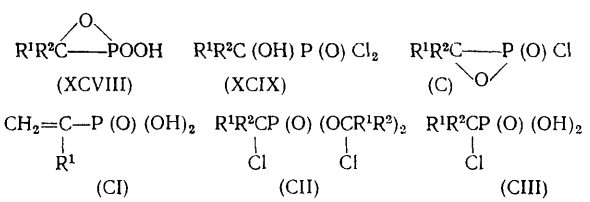


(V)

Approximately 15 years ago, it was assumed that whatever the pathway (*a* or *b*) followed in the synthesis, the mechanism of the formation of compounds (V) is the same: the interaction of the phosphorus(III) chloride with the carbonyl compound leads initially to an adduct, which is then acted upon by the hydrolysing agent.

However, the mechanisms of the interaction of these reactants via pathways *a* and *b* are fundamentally different.

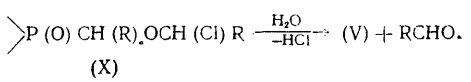
We shall deal briefly with the evolution of views on the reaction of phosphorus(III) chlorides with carbonyl compounds involving the subsequent employment of hydrolysing agents (pathway *a*). According to Michaelis, the adduct (I) hydrolyses directly to the acid (V) (see Scheme 1).[4] Conant assumes the intermediate formation of phosphonic acid (XCVIII).[130,131,133] Careful kinetic studies led him to the conclusion that the hydrolysable reactants interact with the dipolar adduct (II).[6] When acetic acid is employed, the acid chlorides (XCIX) and (C) are formed initially and are converted into the acid (V) on treatment with water. The reaction with ketones is complicated by the formation of the unsaturated acids (CI).[130,132] The mechanism of the interaction of phosphorus(III) chlorides with unsaturated ketones is treated similarly.[6,120,130,131,133]



(XCVIII) (XCIX) (C) (CI) (CII) (CIII)

According to the ideas of Page[7] and Kabachnik,[1] the primary product (III) containing phosphorus(III) isomerises to compound (CII), which subsequently hydrolyses to the acids (CIII) and (CV). In later investigations, Kabachnik[90,134] rejected the possibility of the transition (CIII) → (V) under mild conditions.

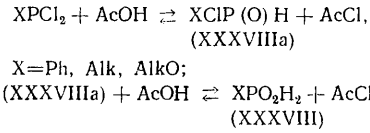
At the present time, the views described above on the reaction pathway *a* are apparently of only historical value. In reality, 1-(1-chloroalkoxy)alkyl derivatives of phosphorus(IV) (X) are formed initially and are subsequently hydrolysed to the acid (V).



(X)

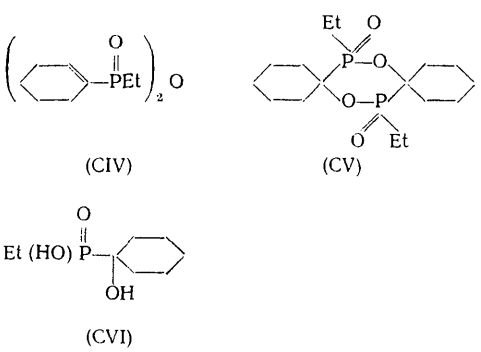
Ketones, which are less reactive than aldehydes, react sluggishly with phosphorus(III) chlorides under mild conditions: in the course of 20–40 h at room temperature.[56,57] Therefore, even if the hydrolysing agent is added to the mixture of phosphorus(III) chloride and the ketone several hours after they have been mixed, pathway *a* hardly makes a decisive contribution to the overall reaction mechanism. Furthermore, in contrast to aldehydes, the interaction of phosphorus(III) chlorides with ketones leads to the formation of different organophosphorus compounds depending on the structure of the ketones: (XXXIII), (XXXV), (XXXVII), and (XXXIX) (Scheme 4), which are entirely stable in relation to hydrolysing agents. On the other hand, in the presence of the latter, the reaction is very rapid (pathway *b*) with formation of compounds (XXXIX) in high yields. Hence it follows that in the case of ketones the adducts (I) and (II) and compound (CII) are not the direct objects of the action of hydrolysing agents.

Mainly as a result of the work of Soviet chemists, it can now be regarded as demonstrated that pathway *b* involves the primary interaction of phosphorus(III) chlorides with the hydrolysing agent and the intermediate formation of hydrophosphoryl compounds (XXXVIII) [in particular, the extremely reactive partial chlorides of phosphonous and phosphorous acids (XXXVIIIa)].[59,61–64,69,70,135–150] When carboxylic acids are used as hydrolysing agents,[70,142] the phosphorus(III) chloride is initially converted into the partial acid chloride (XXXVIIIa), which is capable of hydrolysing further to the acid (XXXVIII). The latter interacts both with the initial phosphorus(III) chloride and with the acyl chloride to form compound (XXXVIIIa). When water is used, the reactions are irreversible.



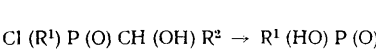
(XXXVIIIa) (XXXVIII)

Carbonyl compounds constitute a kind of trap for active hydrophosphoryl compounds, especially the partial acid chlorides (XXXVIIIa). Cyclohexanone proved to be the most successful carbonyl compound, which made it possible to isolate the product (XXXIXa) in a pure form as a result of its direct interaction with compound (XXXVIIIa, X = Ph).[58,59,139,140] When Ph is replaced by Et in compound (XXXIXa), its stability falls and after the removal of the solvent only the organophosphorus compounds (CIV)–(CVI) are produced.[140,145]



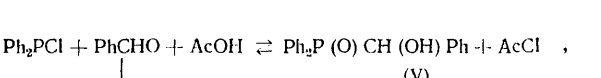
(CIV) (CV) (CVI)

It has been shown recently that compounds (XXXIX) change after a time, being converted into the acid (CIII) containing a 1-chloroalkyl group.[151–153]



(XXXIX) (CIII)

There are also literature data showing that even compounds without a labile P–Cl bond may be modified, for example, compound (V). Thus Miller and Stewart,[154] who repeated Conant's experiments on the interaction of chlorodiphenylphosphine with benzaldehyde in the presence of acetic acid, established that the expected product (V) is initially formed rapidly (5 min) but after three days the final reaction product is not compound (V) but the acetate (CVII) and the diphosphorylated ester (XII):



(V) (CVII) (XII)

The substance characterised by Conant as compound (V)[135] turned out to be the ester (XII).

The reaction of aryldichlorophosphines with ketones in the presence of monothioacetic acid takes place in a somewhat unusual manner:[155] instead of the expected 1-hydroxyalkylphosphinomonothioic acids, 1-mercaptoalkylphosphinic acids (CVIII) are obtained. Since the coordination number of phosphorus remains unaltered in the initial stage of the reaction, the following reaction mechanism has been proposed:

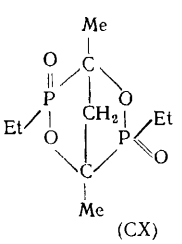
$$PhPCl_2 + CH_3COSH \xrightarrow{HCl} PhP(Cl)SCOCH_3 \xrightarrow{R^1R^2C=O} \rightarrow R^1R^2C(Cl)P(O)(SCOCH_3)Ph \xrightarrow{H_2O} R^1R^2C(SH)P(O)(OH)Ph.$$
(CVIII)

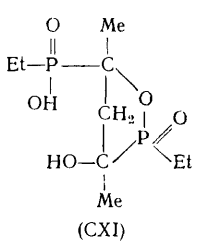
The interaction of phosphorus(III) chlorides with aldehydes and ketones in the presence of mercaptans is a new convenient method of synthesis of α-alkylthioalkylphosphonates and the corresponding phosphinates (CIX).[156]

$$R^1R^2PCl + R^3R^4C=O + R^5SH \xrightarrow{-HCl} R^1R^2P(O)CR^3R^4(SR^5).$$
(CIX)

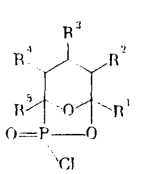
The reactions of phosphorus(III) chlorides with unsaturated ketones in the presence of hydrolysing agents also includes a stage involving the formation of hydrophosphoryl compounds (XXXVIII).[69,157] If hydrogen sulphide is used instead of acetic acid or water, products with the thiophosphoryl group are obtained.[158]

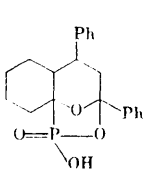
The reactions of diketones with phosphorus(III) chlorides in the presence of acetic acid have also been investigated.[159–163] The reaction of chloroethylphosphine and actylacetone leads to the formation of the bicyclic diphosphorus compound (CX), which hydrolyses very readily to the monocyclic derivative of 2-oxa-1,2-oxaphospholan (CXI).[159]

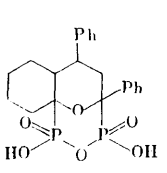

(CX)


(CXI)

Monophosphorylated [compounds (CXII) and (CXIII)] and diphosphorylated [compound (CXIV)] derivatives of tetrahydropyran are formed from PCl_5 and 1,5-diketones:[160–163]

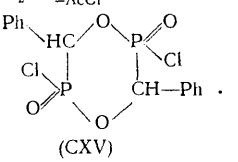

(CXII)


(CXIII)


(CXIV)

A hydrolysing agent, can also be used in the synthesis of polyfunctional organophosphorus compounds from a phosphorus(III) chloride, a carbonyl compound, and a dialkylamine[164,165] or the amides of carboxylic and carbonic acids.[166–176] It is suggested that the reactions proceed via a stage involving the formation of hydrophosphoryl compounds.[172]

New data have also been obtained in the study of the reactions of phosphorus(III) chlorides with aldehydes in the presence of acetic anhydride.[8,177] The authors were able to isolate the cyclic product (CXV), which is assumed to be a precursor of compound (V), obtained by the hydrolysis of the adduct of the aldehyde with the phosphorus(III) chloride. A mechanism including the initial interaction of PCl_3 with the aldehyde was postulated initially:[8]

$$PhCHO + PCl_3 \rightleftarrows PhCH(Cl)OPCl_2 \xrightarrow[-AcCl]{Ac_2O} \rightarrow PhCH(OCOCH_3)P(O)Cl_2 \xrightarrow{-AcCl}$$

(CXV)

This mechanism is incorrect, because, as shown above (see Section II), not one but two aldehyde molecules should be consumed per P–Cl bond.[16–18,22–24] It was later established that aldehydes react initially with acetic anhydride to form the diacetate (CXVI), PCl_3 functioning as the process catalyst.[177,178] The subsequent reaction of the diacetate with PCl_3 leads to compound (CXV). It was obtained by unambiguous synthesis from compound (CXVI) and PCl_3 and also from compounds (XVII) and (CXVII):

$$PhCHO + Ac_2O \xrightarrow{PCl_3} \underset{(CXVI)}{PhCH(OAc)_2} \xrightarrow{PCl_3} \underset{(CXVII)}{PhCH(OAc)Cl} + AcOPCl_2 \rightarrow$$
$$\rightarrow \underset{(XVII)}{(POCl)_n} + AcCl + (CXVII) \rightarrow (CXV).$$

However, not everything is clear in this mechanism. The structure of the product (XVII) has not been established and it has not been shown what are the essential features of the catalysis and whether or not compound (XVII) does really react on treatment with compound (CXVII) in accordance with the mechanism of the Arbuzov reaction (since α-chloroalkyl carboxylate esters are weak electrophiles). The mechanism of the interaction of phosphorus(III) chlorides with ketones, including unsaturated ketones, in the presence of acetic anhydride has not been finally elucidated, although in the case of unsaturated ketones we have an important general method of synthesis of compounds with the 1,2-oxaphospholene ring[2,179–183] and the latter can be used to synthesise ketoalkyl esters of phosphorus acids.[2,184–187]

The procedure in which the reactions of phosphorus(III) chlorides with carbonyl compounds are carried out in the presence of phosphorus(III) acid esters proved to be fruitful.[40] Such reactions were first achieved by Birum.[188] Organic compounds containing several phosphorus atoms different coordination numbers have been obtained by this procedure. It is believed that the phosphorus(III) acid ester initially adds to the carbon atom of the carbonyl group with formation of the dipolar ion (CXVIII),[40] whose interaction with the phosphorus(III) chloride leads to the polyfunctional compounds (CXIX):

$$(3-n)\ R^1R^2POR^3 + (3-n)\ R^4R^5C{=}O \rightarrow (3-n)\ R^1R^2\overset{+}{P}(OR^3)-\underset{R^5}{\overset{R^4}{C}}-O^- \xrightarrow{+R^6_nPCl_{(3-n)}} \rightarrow$$

(CXVIII)

$$\rightarrow R^6_nP\,[OCR^4R^5P\,(O)\,R^1R^2]_{3-n} + (3-n)\ R^3Cl.$$

(CXIX)

In recent years, these reactions were used to obtain acetals containing two phosphorus atoms with different coordination numbers[189,190] and the monophosphorylated [compound (CXX)] and diphosphorylated [compound (CXXI)] alkyl phosphorodichloridites:[191,192]

$$R^1CHO + P\,(OR^2)_3 + PCl_3 \rightarrow (R^2O)_2\,P\,(O)\,CHR^1OPCl_2 + R^2Cl,$$

(CXX)

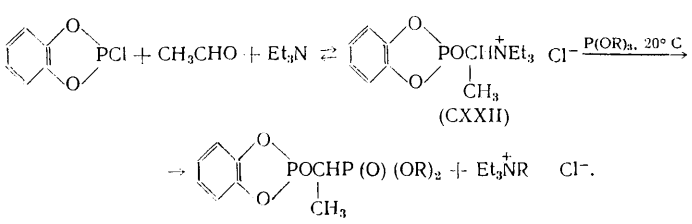
$$(R^1O)_2\,P\,(O)\,COCH_3 + P\,(OR^2)_3 + PCl_3 \rightarrow (R^1O)_2P(O)-\underset{O{=}P\,(OR^2)_2}{\overset{O\quad CH_3}{\overset{\|\quad|}{C}}}-OPCl_2 + R^2Cl.$$

(CXXI)

The replacement of trialkyl phosphites in this process by their thioanalogues alters fundamentally the character of the reaction:[193]

$$(R^1S)_3\,P + R^2R^3C{=}O + PCl_3 \rightarrow Cl_2P\,(O)\,\underset{SR^1}{CR^2R^3}.$$

Fairly numerous studies have been devoted to the reactions of phosphorus(III) chlorides with carbonyl compounds in the presence of triethylamine in order to synthesise unsaturated organophosphorus compounds. The synthesis of vinyl esters of phosphorus(III) acids by the reaction of *o*-phenylene and ethylene phosphorochloridites with acetaldehyde in the presence of triethylamine was reported as early as 1957.[194] The salt (CXXII) is formed initially in these reactions, its vacuum heat treatment affording the vinyl ester. However, further study of this reaction showed that, under conditions described in the above study,[194] the salt (CXXII) decomposes into the initial compounds, *o*-phenylene phosphorochloridite being isolated in a satisfactory yield. In the presence of trialkyl phosphite, the salt (CXXII) decomposes under mild conditions with formation of compounds (CXXIII) containing two phosphorus atoms:[29]



(CXXII)

(CXXIII)

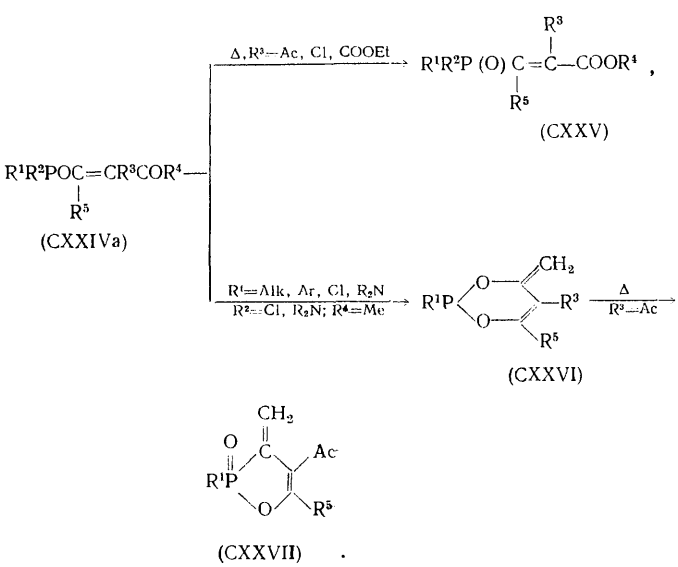
It has been established that electron-accepting substituents at the phosphorus(III) atom and the α-carbon atom of the ketone favour reactions involving the formation of a wide variety of unsaturated organophosphorus compounds (CXXIV):[81,82,91,100,195–224]

$$R_nPCl_{3-n} + (3-n)\ O{=}CCHYZ \xrightarrow[-(3-n)Et_3N\cdot HCl]{(3-n)Et_3N} R_nP\,(OC{=}CYZ)_{3-n}.$$

(CXXIV)

Base catalysis apparently operates in this instance and the intermediates are triethylammonium enolates. This has been confirmed indirectly by the interaction of both phosphorus(III) and phosphorus(IV) chlorides with ketones exhibiting an enhanced CH acidity under comparable conditions. For comparison, one should note that, depending on the structure of the ketone and the nature of the substituents at the phosphorus(III) atom and the solvent, sodium enolates give rise not only to unsaturated compounds but also to *C*-phosphorylated derivatives as well as *OC*-diphosphorus compounds.[225–228]

In the case of β-dicarbonyl compounds, the substitution products (CXXVIa) can be isolated in a pure form,[82,210–219,222] while in the presence of a base many of them are converted into the cyclic derivatives (CXXVI).[80,206–212,215,216] On heating, compounds (CXXIVa) and (CXXVI, R^3 = Ac) undergo the vinyl phosphite–vinyl phosphonate rearrangement with formation of compounds (CXXV) and (CXXVII):[214,215,218,223]



(CXXV)

(CXXIVa)

(CXXVI)

(CXXVII)

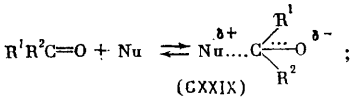
In the case of thiocyanatoacetone, the substitution product (CXXIVb) cyclises to 1,3,2-oxathiaphospholene (CXXVIII) with elimination of propionitrile:[209]

$$(EtO)_2\,POC{=}CHSCN \rightarrow \underset{O}{\overset{S}{\square}}P\,(O)\,OEt + EtCN.$$

(CXXIVb) (CXXVIII)

Important results have been obtained using as the third reactant an alkyl vinyl ether (AVE), which is a weaker nucleophile than trialkyl phosphites and triethylamine. The latter activate the carbonyl compound and enter unchanged into the composition of the final products (CXXII) and (CXXIII), forming a new C–E bond (E = P, N).[188,194] In contrast to them, alkyl vinyl ethers

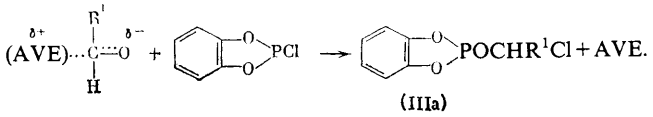
activate only the carbonyl group in aldehydes, without forming a new C–C bond and do not enter into the composition of the reaction product.[29,30,229] The fact that all the nucleophiles enumerated block the carbon atom of the carbonyl group as a result of the formation of the donor–acceptor complex (CXXIX) and hence also the carbonium ion centre in the intermediate adduct (XIV) is also an important feature. This is apparently in fact the cause of the consumption of only one molecule of the carbonyl compound per P–Cl bond in the presence of these nucleophiles.



(CXXIX)

Nu = $P(OR)_3$, Et_3N, AVE.

Only by creating special conditions has it been possible to achieve the synthesis of one of the representatives of the primary adducts of phosphorus(III) chlorides with aldehydes (IIIa),[29,30,229–231] the possibility of the formation of which had been predicted at an early stage by Page[7] and then by Kabachnik[1] and Atherton.[8]



(IIIa)

In the absence of an alkyl vinyl ether, the product (IIIa) decomposes slowly into the initial compounds, the latter forming an adduct in proportions of 1 : 2.

IV. Conclusion

The main conclusion arising from the data described is that, in the case of PCl_3 and phosphorus(III) dichlorides, the primary process in the interaction with carbonyl compounds can be characterised as catalytic nucleophilic substitution at the electrophilic phosphorus(III) atom, the admixture of HCl in the phosphorus(III) chlorides playing the role of the catalyst under these conditions. In various secondary processes, the coordination number of phosphorus rises to 4. Depending on the nature of the carbonyl compound, the roles of both a nucleophile and an electrophile are attributed to secondary chlorophosphines and phosphorochloridites. However, additional studies are required for a more correct solution of this problem.

Ketones are less reactive than aldehydes, but their reactions with phosphorus(III) chlorides are more varied. More far reaching studies are required to establish the true nature of the processes leading to specific compounds. In the presence of a secondary functional group in the ketone, the more reactive group reacts with the phosphorus(III) chloride and subsequently the primary product participates in various intramolecular and intermolecular interactions with formation of important polyfunctional organophosphorus compounds. The reactions of phosphorus(III) chlorides with aldehydes and ketones in the presence of hydrolysing agents are characterised by the conversion of phosphorus(III) chlorides into hydrophosphoryl compounds and the addition of the latter to the carbonyl group. Tertiary amines, trialkyl phosphites, and alkyl vinyl ethers, used as the third reactant, do not increase the coordination number of the phosphorus atom linked initially to the chlorine atom. Depending on the structure of the carbonyl compound, base or nucleophilic catalysis operates. An alkyl vinyl ether makes it possible to synthesise the primary products of the interaction of phosphorus(III) chlorides with aldehydes in proportions of 1 : 1. The question of the synthesis of intermediates with phosphorus(III) and two aldehyde fragments per P–Cl bonds still remains open.

A satisfactory answer cannot be found in the literature for all the questions raised. In view of both the theoretical importance of these reactions and their importance in the development of preparative syntheses of organophosphorus compounds with functional group substituents, there has been an increasing growth of interest in these processes. The present review surveys the advances in the development of this field and is also designed to draw the attention of investigators to a number of problems which are still unsolved.

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The azinyl–azinylidene tautomerism of azinylmethanes and general problems of the tautomerism of azines

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ABSTRACT. The results of studies on the tautomerism of azinylmethanes are surveyed. The terminology, the structure of the tautomeric forms, the thermodynamics and mechanisms of their interconversion, the dependence of the equilibrium on structure factors and the character of the medium, and certain general characteristic features of tautomeric equilibria of the azinyl–azinylidene type are discussed.

The bibliography includes 127 references.

Contents

I. Introduction 268
II. The [1,3]sigmatropic tautomerism of azinylmethanes 270
III. Intrachelate [1,5]sigmatropic tautomerism of substituted methylazines 272
IV. Thermodynamics, kinetics, and mechanism of tautomeric interconversions of azinylmethanes 274
V. The influence of the solvent and structural factors on the tautomerism equilibria of the azinyl–azinylidene type 277

I. Introduction

The tautomerism of organic compounds is an important branch of organic chemistry with an interesting history and tradition, the interest in which has been sustained also in recent years.[1–3] It is possible to differentiate three main problems which have stimulated the interest in tautomerism.

1. The dependence of the structure and physical properties of the compounds on their tautomeric composition
2. The inter-relation between tautomerism and reactivity.
3. The search for and construction of tautomeric molecules with properties of practical importance (photochromic systems, models of enzyme active centres, rearranging molecules).

Since prototropism is as a rule associated with the heteroatomic groups OH, NH, SH, etc., it is not surprising that tautomeric equilibria are encountered particularly frequently in heterocyclic compounds. The structure and physical and chemical properties of the latter are frequently difficult to understand if their tautomeric characteristics have not been elucidated. It is not fortuitous that virtually every chapter in modern monographs on the chemistry of heterocyclic compounds (see, for example, Barton and Ollis[4]), devoted to a particular class of heterocyclic compounds, includes also a section on tautomerism. The tautomerism of azine derivatives† (Scheme 1), whose fundamental character has been emphasised in an extensive monograph[3] in connection with the study of the structure of DNA, is especially important. The tautomerism of azines has also been discussed in connection with the problem of enzyme catalysis,[6] in the study of the reactivity on internal factors and medium effects,[7] etc.

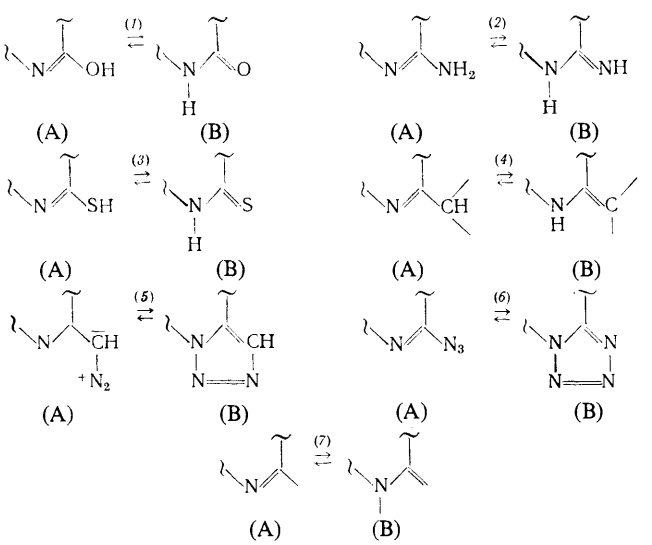
Scheme 1 presents the principal types of tautomeric equilibria observed in the series of azine derivatives as a function of the character of the exocyclic fragment undergoing tautomerism. Among equilibria of types (*1*)–(*6*), the tautomerisms of hydroxyazines [equilibrium (*1*)] and aminoazines [equilibrium (*2*)] have been most completely studied, which is to a significant extent due to their biochemical importance. An important difference of the tautomeric equilibria of azinylmethanes consists in the fact that the rate of dissociation of the CH bond is significantly lower than those of the OH, NH, or SH bonds. This increases the lifetime of the tautomers and makes it possible to use the NMR method effectively. Its application to equilibria (*1*)–(*3*) is hindered by the proton exchange, which is rapid on the NMR time scale. Thus, apart from their independent interest, azinylmethane derivatives can also serve as key models for the search for and formulation of general characteristics of the tautomerism of the azinyl–azinylidene type: (A) ⇄ (B).

The tautomerism of substituted methylazines[4] has not so far been the subject of a special review. Admittedly there exists a monograph[3] in which the literature up to 1975 is presented, but the very character of the monograph precluded a detailed treatment of the analysis of such tautomeric molecules. Furthermore, during the

† There is some uncertainty as to which compounds should be classified as azines. If a formal standpoint and nomenclature are adopted as a basis, then the group of azines will include, together with diazines, triazines, and tetrazines, also, for example, thiazines but not pyridine (see, for example, the Chemical Encyclopaedic Dictionary).[5] On the other hand, from a non-formal point of view, pyridine is in many respects closer to diazines and triazines than are oxazines or thiazines. Bearing in mind the chemical similarity, there is a genuine need for differentiating the group of six-membered heteroatomic compounds—benzene analogues where one of several –CH= groups have been replaced by a nitrogen atom –N=. It would be useful to adopt firmly the term "azines" for this particular group of compounds. We may note that in a recent fundamental publication[4] the section on azines included pyridine and its analogues but did not deal with nitrogen-containing cyclic compounds with oxygen, sulphur, etc.

last ten years numerous important data on the tautomerism of substituted methylazines have been published. The present review deals with studies on the prototropic tautomerism of azinylmethanes (up to 1988) as well as certain general features characteristic of both the tautomerism of azinylmethanes and and azinyl-azinylidene tautomerism as a whole. We endeavoured to restrict the treatment to derivatives based on the aromatic ring of azines or their condensed benzo-analogues. We shall not discuss in detail in this review the relation between tautomerism and reactivity, although important studies in this field have been published recently.[7,8] Nevertheless, it is essential to emphasise the methodological relation between the study of tautomeric and chemical properties in relation to a class of potentially tautomeric compounds such as azinylmethanes, hydroxyazines, etc. A series of studies have been published[9] on tautomerism and dual reactivity, where it was shown that the phenomenon of dual reactivity is extremely general and is by no means always caused by tautomerism. This conclusion concerning the dual reactivity of tautomeric molecules is frequently treated too broadly and is applied to their reactivity as a whole. Nevertheless, if the class of compounds considered from the standpoint of chemical behaviour exhibits also a tautomeric property, its far-reaching characterisation is impossible without considering such properties. Just as the study of the structure of a chemical compound precedes a complete understanding of its chemical properties, so does the study of the tautomeric structure constitute a necessary basis (stage) for the understanding of the reactivity of compounds exhibiting tautomeric properties.[1]

Scheme 1



For tautomers whose stabilities are close, the relation between the composition of the reaction products in the tautomeric equilibrium is determined by the familiar Curtin–Hammett principle.[2,10] For slow (relative to the reaction rates) tautomeric interconversions, the composition of the product is predetermined by the tautomeric equilibrium constant K_T. For "fast" reactions, no direct relation between the structure of the tautomers and the composition of the reaction products may be observed. Nevertheless, in these cases too it is necessary to understand the tautomeric characteristics if only to be able to elucidate which of the tautomeric forms is responsible for the formation of the products.

It is likewise noteworthy that the range of energies corresponding to the contents of the tautomers being compared is very narrow ($\Delta G \simeq 0-5$ kcal mol^{-1}) and the chemist frequently deals with potentially tautomeric compounds existing almost wholly in one form or another. Although in this case one may speak of the absence of tautomerism, nevertheless the study of such systems is undoubtedly essential in the investigation of tautomerism from general standpoints. The specific properties of individual tautomers whose reactivities, generally speaking, differ radically can be most fully manifested under these conditions. In the case of a marked difference between the chemical properties of the tautomers, the specific fixation or displacement of the equilibrium to one side or another (for example with the aid of methylation, by means of structural factors, medium effects, complex formation, and irradiation) can be one of the ways of regulating the reactivity of compounds.

Thus the knowledge of the tautomeric properties of compounds not only helps to explain and predict their chemical properties but also provides a possibility for regulating them.

The main types of tautomeric interconversions (*1*)–(*6*) in series of azines (Scheme 1) can be combined on the basis of the characteristic rearrangement of bonds [equilibrium (*7*)]. The two principal features of this rearrangement are the change in the hybridisation of the nitrogen atom from the "pyridine" type to the "pyrrole" type ("amide" type) and the change in the multiplicity of the exocyclic bond involved in the tautomeric transformation.

In the classification of equilibria of types (*1*)–(*6*), one usually adopts as a basis the structure of the exocyclic group, for example, the "hydroxy–oxo" tautomerism of hydroxyazines (1), the thiol–tautomerism of mercaptoazines (2), etc. In those cases where it is necessary to differentiate the general features of a family of equilibria, it is also logical to base the treatment on the structural characteristics of the azine component of the molecule, treating it as a substituent in relation to the exocyclic fragment. Using the IUPAC nomenclature for naming the azine groups, we shall if necessary refer henceforth to equilibria of type (A) ⇄ (B) as pyridyl–pyridylidene and pyrimidyl–pyrimidylidene tautomerisms or in the general case the azinyl–azinylidene tautomerism (which can be shortened to azinyl–ylidene or azaheteroaryl–ylidene tautomerism). The names proposed above can be applied not only to the sigmatropic tautomerism[11] of type (*1*)–(*4*), associated with the migration of a proton, but also to the tautomerism of the electrocyclic type [equilibria (*5*) and (*6*)], where the topology of the change in the bonds also satisfies the conditions mentioned above. Within this family, it is useful to employ the general classification of tautomeric processes.[11] Almost all the processes examined below are [1,*j*]sigmatropic rearrangements where it is possible to identify an atom or group whose position is altered ("migrant") and the remainder of the molecule ("skeleton").[12]

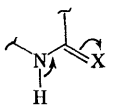
For heterocyclic molecules, synchronous or multistage processes with participation of two (or more) migrating groups are common.[2,3,13] The term "diotropic transformations" proposed previously[14] appears inadequate in this instance, because it is firmly related to the type of mechanism of the interconversion. Potentially tautomeric molecular systems with two and more migrating groups can be more conveniently classified as di-(tri-, etc.)sigmatropic systems, while the corresponding type of equilibria, where the different forms differ by the positions of two migrating groups, can be referred to as disigmatropic equilibria.[15]

In view of the lack of firm boundaries between the phenomena of tautomerism and isomerism, there should exist some consistency in

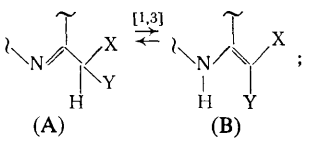
the terminology employed. Thus, taking into account the analogy of the pairs of terms "isomerism"—"isomerisation" and "tautomerism"—"tautomerisation" (the latter expression will be used to designate the tautomeric rearrangement (A) ⇄ (B) (but not the equilibrium).

II. The [1,3]sigmatropic tautomerism of azinylmethanes

The tautomeric equilibrium of unsubstituted azinylmethanes (A) ⇄ (B) is fully displaced to form (A). Judging from experimental data, the relative capacity of substituted azines for transition to form (B) increases in the series of exocyclic groups CH < NH < OH, which apparently reflects the stabilisation which arises when the endocyclic NH group is conjugated with the C=C, C=N, and C=O fragments respectively:[16]



As in the case of aminoazines,[17,18] the appearance of the ylidene tautomer in the series of azinylmethanes is promoted by electron-accepting substituents in the exocyclic fragment:[16,19]

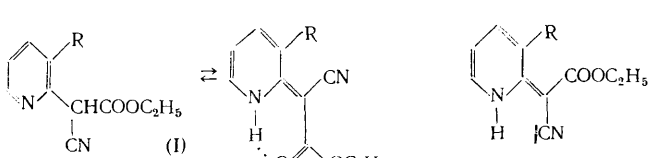


(A) (B)

X = Y = CN, NO_2, COOR, SO_2R, $C_6H_4NO_2$.

Type (4) tautomerism was apparently first mentioned by Chichibabin in 1918.[20] A little later he succeeded in observing tautomeric forms of types (A) and (B) for dinitrobenzylpyridine.[21] During the same years, tautomerism was observed in the series of pyridylmethanes[22] and quinolinylmethanes,[23,24] whose study was subsequently continued.[25]

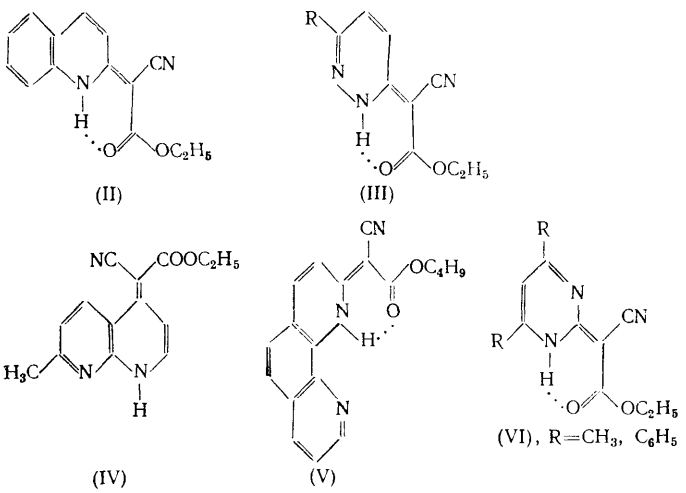
In the series of substituted CH-azines, the tautomerism of azinylcyanoacetic esters has been studied in fair detail. Thus, according to ^{1}H NMR spectroscopic data obtained in $CDCl_3$,[26] pyridyl-2-cyanoacetic ester (I, RH) is in the ylidene form (B) (δ_{NH} = 14.1 p.p.m.). For the analogous 3-methyl derivative, it has been suggested[27] on the basis of ^{1}H NMR spectra that the non-chelate ylidene tautomer (B′) (R = CH_3) is formed. It may be that, in view of the low rate of the tautomeric interconversion, form (B′) was observed by the authors[27] under non-equilibrium conditions. The formation of thermodynamically stable non-chelate tautomers requires special conditions, for example, basic solvents, which stabilise the form of type (B′) as a result of the formation of an intermolecular hydrogen bond (HB).



(A) (I) (B) (B′)

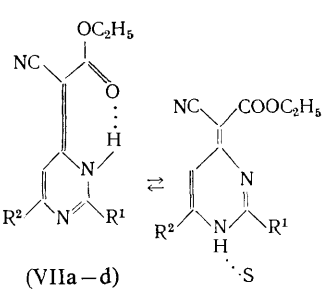
Thus the use of dimethyl sulphoxide (DMSO) as the solvent led to the formation of significant amounts of non-chelate ylidene forms in the case of substituted pyrimidinyl-2-cyanoacetic esters.[28]

Quinolinylcyanoacetic ester (II) [29,30] and the analogous pyridazine (III),[30] pyrazine,[31] naphthyridine (IV),[32] and phenanthroline (V) [29] derivatives, obtained by the reaction of the corresponding *N*-oxides or halogeno-derivatives with cyanoacetic ester, exist in the ylidene tautomeric form. The latter predominates also for pyrimidinyl-cyanoacetic ester (VI), whose structure was examined by Zagulyaeva and Mamaev[33] and was later proved by UV spectroscopy.[34]



(II) (III) (IV) (V) (VI), R=CH_3, C_6H_5

In the case of cyanoacetic derivatives of di- or tri-azines, several types of ylidene tautomers can be produced. Thus, 4-pyrimidinyl-cyanoacetic esters (VII) can form ylidene tautomers with the *ortho*- and *para*-quinonoid disposition of the double bonds in the heterocycle. Both tautomers of 2-methylpyrimidinyl-4-cyanoacetic ester (VIIb) were isolated in a pure state (solid phase).[35] It was shown that in solvents of low polarity the *ortho*-quinonoid tautomer is more stable; the formation of the *para*-quinonoid tautomer is promoted by polar media and solvents forming hydrogen bonds.[36,37]



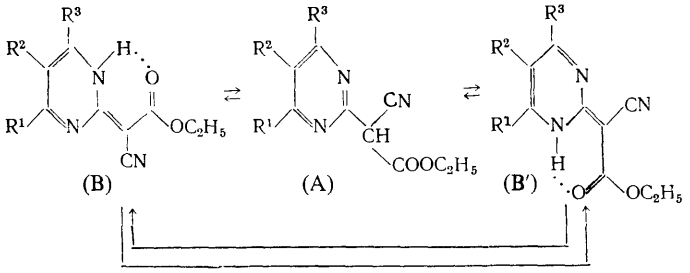
(VIIa–d)

(VIIa): $R^1 = R^2 = H$;
(VIIb): $R^1 = CH_3$, $R^2 = H$;
(VIIc): $R^1 = CF_3$, $R^2 = H$;
(VIId): $R^1 = H$, $R^2 = C_6H_5$.

The stabilisation of the *para*-quinonoid tautomer by polar solvents was also observed for the unsubstituted 4-pyrimidinyl-cyanoacetic ester (VIIa) and its trifluoromethyl analogue (VIIc). The steric hindrance in 6-phenyl-4-cyanoacetic ester (VIId) prevents the formation of the *para*-quinonoid tautomer either in DMSO, or in hexamethylphosphoramide (HMPA), or in the crystalline state.[35]

Two types of ylidene tautomers (B) and (B′) have been detected for pyrimidinyl-2-cyanoacetic esters (VIII) substituted asymmetrically in the pyrimidine ring. Analysis of the spin–spin coupling of the ring protons in the ^{1}H NMR spectrum made it possible to distinguish reliably these forms and to determine the ratios of the forms (A), (B), and (B′).[28] For example, 2% of the tautomer (A),

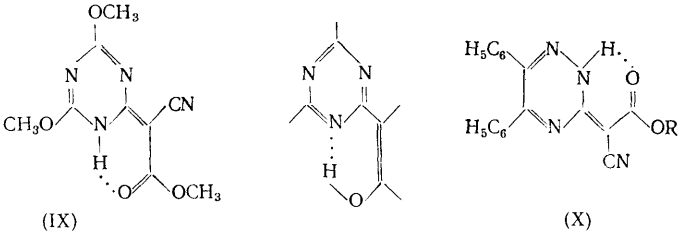
70% of the tautomer (B), and 28% of the tautomer (B′) were detected for the pyrimidinylcyanoacetic ester (VIIId) in $CDCl_3$.[28] The occurrence of the degenerate tautomeric transformations of the type (B) ⇄ (B′) ($R^1 = R^3 = H$) was established by a pulse mode double resonance ^1H NMR study using transfer of a saturation label.[28,38]



(B) (A) (B′)

(VIIIa): $R^1 = R^2 = R^3 = H$; (VIIIb): $R^1 = R^3 = H$, $R^2 = OCH_3$; (VIIIc): $R^1 = R^3 = H$, $R^2 = N(CH_3)_2$; (VIIId): $R^1 = C_6H_5$, $R^2 = R^3 = H$.

Among 1,3,5-triazine derivatives, the tautomerism of the dimethoxy-derivative (IX) was studied in greatest detail.[39] It exists in $CDCl_3$ predominantly in the ylidene tautomeric form. Traces of the aromatic form (A) of this compound were detected by IR spectroscopy (the change to a hexane solution entails an increase in the content of this tautomer[38]). It has been assumed[39] that the enolic tautomer of compound (IX), involving an enolised ester group, exists. However, from ^{14}N NMR data, it has been shown[28,40] that an appreciable amount of the enolic tautomer is not formed in cases of this kind. The signal of the NH group observed in the ^{14}N NMR spectrum (−260 p.p.m. relative to CH_3NO_2) is typical for nitrogen of the amide type;[41] on the other hand, in the case of enolisation, a downfield shift of the signal should have been observed (−100 p.p.m.). 1,2,4-Triazinylcyanoacetic ester (X) also exists in the ylidene tautomeric form.[42]

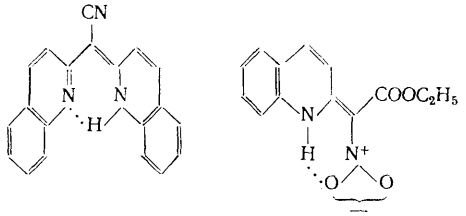


(IX) (X)

^{14}N NMR	−260 p.p.m. (exp.)	−100 p.p.m. (expected value)

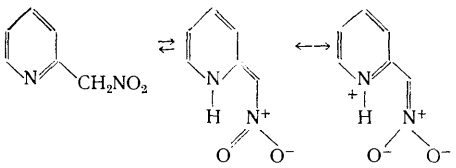
Thus, the ylidene tautomer of cyanoacetic acid derivatives of unsubstituted azines is as a rule more stable than the aromatic tautomer. The aromatic tautomers have been detected in trace amounts only for pyrimidinyl-2-cyanoacetic and pyrazinyl-2-cyanoacetic esters.[28,31] The presence of a cyclic substituent affects appreciably the position of the tautomeric equlibrium and in many cases the content of forms (A) and (B) may prove to be comparable, as happens, for example, for 5-methoxy- or 5-dimethylamino-pyrimidinyl-2-cyanoacetic esters (VIIIb, c).[28]

In the series of azines, the structure of malonodinitrile derivatives has also been studied. Regardless of the nature of the heterocycle, malonodinitrile derivatives exist in the ylidene tautomeric form.[19,27,29–31,33,34,43–46] The lower electron-accepting capacity of the COOR group compared with the nitrile group is responsible for the lower tendency of azinylmalonic ester to be converted into the ylidene form. The aromatic tautomer of azinylmalonic esters is usually more stable.[34,47–49] However, in certain cases, for example for pyridinyl-4-malonic and pyridazinyl-3-malonic esters, the contents of the tautomers (A) and (B) were comparable.[50] The azinyl−azinylidene tautomeric equilibrium occurs for bisquinolinylmethanes of type (XI)[51,52] and derivatives of nitroacetic ester (XII).[30]



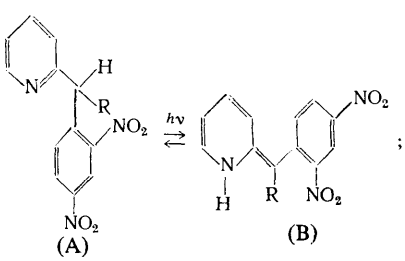
(XI) (XII)

The substituted azinylmethanes examined above contain two electron-accepting substituents at the CH fragment, but the presence of only one acceptor is sometimes sufficient for the occurrence of an equilibrium of type (A) ⇄ (B). Thus, in the nitration of a large series of methylazines, it has been observed that the nitromethylazines (XIII) obtained in this process are capable of the (A) ⇄ (B) tautomerism.[53] (It is noteworthy that the representation of the ylidene tautomer in the above study by another resonance formula does not alter the essential features of the situation. It is essential not to confuse resonance representations of the same ylidene tautomer with the tautomeric equilibrium itself.)



(A) (B) (XIII)

The ylidene tautomers of certain azinylmethanes are kinetically stable and can be formed, in particular, under the influence of UV irradiation. Among such compounds, derivatives of *o*-nitrobenzyl type are best known.[54] After the irradiation of compound (XIV), the appearance of a coloured ylidene form is observed. It undergoes thermal tautomerisation to the starting material.[55] With increase in the electron-accepting capacity of the substituent at the CH fragment, the equilibrium (A) ⇄ (B) occurs even in the ground state. Thus for compound (XV) in $CDCl_3$ such equilibrium was established by ^1H NMR and UV spectroscopic methods.[56]



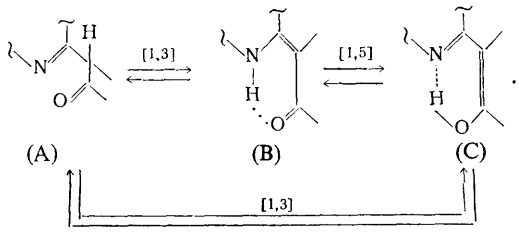
(A) (B)

(XIV): R = H; (XV): R = $COOCH_3$.

In this case too, irradiation increases the fraction of the tautomer (B), i. e. one may speak of an example of a photosensitive equilibrium of the azinyl–azinylidene type.[56] (A detailed discussion of the photoinduced tautomerisation of the azinyl–azinylidene type is outside the framework of the present review.)

III. Intrachelate [1,5]sigmatropic tautomerism of substituted methylazines

The compounds examined above are characterised by a low tendency towards a tautomeric rearrangement of the substituents in the exocyclic group. More favourable possibilities for tautomerism in the side chain are provided by acyl groups, which constitute the basis of the most frequently encountered tautomeric equilibria of the keto–enol type. The structure and tautomerism of acylmethylazines (including the simplest representative 2-acetonylpyridine) have been the subject of a prolonged controversy.[57]

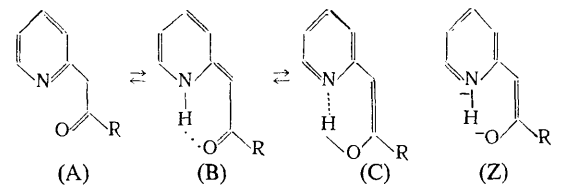


The tautomeric transitions (A) ⇄ (B) and (A) ⇄ (C) are instances of [1,3]sigmatropic tautomerism.[11] Intermolecular proton transfer is characteristic of such processes, while an intramolecular mechanism is unlikely because of symmetry requirements.[58] Since the rate of proton migration between the heteroatom and the carbon atom is usually low,[59] the study of such equilibria by NMR does not present appreciable difficulties in most cases. The intrachelate tautomeric (B) ⇄ (C) transition, an example of the [1,5]sigmatropic tautomerism, occurs, on the other hand, by an intramolecular mechanism characterised by a high rate and the NMR spectra show average signals due to both forms—(B) and (C).[60]

Vigorous investigation of the character of the potential energy surface (PES) for the [1,5]transfer of a proton, carried out in relation to the enolic form of malonodialdehyde (XVI) by both experimental and theoretical methods,[61] showed that the two-well PES profile corresponds to this type of equilibrium (Fig. 1). Since even in this favourable case the one-well potential does not occur, its existence for asymmetric chelates of types (B) and (C) appears unlikely.[62]

A reliable demonstration of the occurrence of the tautomers (B) and (C) (two-well potential) is provided by the spectroscopic identification of both tautomers with the aid of some kind of "rapid" method (IR, UV, and photoelectron spectroscopy, etc.). It is essential to note that formulae with equalised bonds are used not so much to designate a one-well potential surface for this compound but to state the uncertainty in the position of the proton (OH or NH form) (Fig. 1).[63]

Another uncertainty arising when the intrachelate tautomerism is discussed is frequently associated with the fact that in some studies the possibility of the formation of a "zwitter-ionic" tautomer is discussed. Thus, for the pyridine derivatives (XVII), the authors[64] consider also the tautomeric form (Z) together with forms (A), (B), and (C). However, it is easy to see that the formulae (B) and (Z) are merely different resonance designations of the same tautomer.



(XVII): R = CH_3 (a), C_2H_5 (b), C_3H_7 (c), iso-C_3H_7 (d), CF_3 (e), C_6H_5 (f), t-C_4H_9 (g).

In many early studies, the authors considered only two tautomeric forms for compounds of the pyridine series (XVII): the keto-form (A) and the enolic form (C). The possibility of the formation of the ylidene tautomer (B) in the equilibrium mixture was not then discussed.[65,66] For example, the picolinylketones (XVIIa–e)[65] and derivatives of phenylacylpyridine (XVIIf),[66] whose structures had been determined by IR, UV, and ^1H NMR spectroscopic methods, were examined from these standpoints. It was found that the tautomeric composition of the picolinylketones (XVIIa–e) is not correlated with the polarity constants of the substituent R, but there is a satisfactory correlation with the constants E_s reflecting the steric requirements of the substituents.[65] Evidently the neglect of the possibility of the formation of the ylidene tautomer (B) lowers the reliability of the conclusions reached. The tautomerism of the simplest representative of acylmethylazines—2-acetonylpyridine (XVIIa)—has been investigated[67] and the authors took into account all three possible tautomers. Information about the positions of both the "slow" tautomeric equilibria (A) ⇄ (B) and (A) ⇄ (C) and of the "fast" tautomeric equilibrium (B) ⇄ (C) has been obtained with the aid of ^1H NMR. Mondelli and Merlini[67] based their treatment on the fact that allylic interaction of the protons of the methylidyne and methyl groups (J_{CH/CH_3} = 1–2 Hz) should occur in the enolic tautomer (C) of acetonylazines. In the ylidene tautomer, the interaction of these protons takes place across a single bond and is significantly weaker; the corresponding spin–spin coupling constant is assumed to be zero. J_{CH/CH_3} = 0.65–0.75 Hz for acetonylpyridine, which indicates, according to the authors,[67] the predominance of the enolic form in the equilibrium (B) ⇄ (C). It is thought that, as a consequence of the weakness of the spin–spin

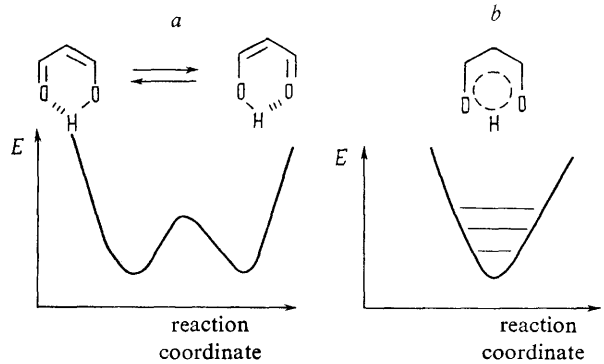


Figure 1. The character of the potential energy surface for two-well (*a*) and one-well (*b*) profiles.

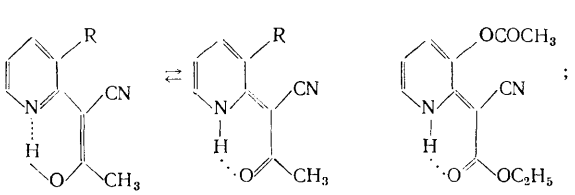
coupling and also because of the lack of rigour of the zeroth approximation for J_{CH/CH_3} in the case of the ylidene form, it is in many cases difficult to use the above criterion, especially for quantitative estimates.

Using ^1H NMR spectroscopy, Klose and Uhlemann[64] examined the tautomerism of ^{15}N-labelled picolinylketone derivatives (XVIId, g). Since $^{15}N-H$ spin–spin coupling was not observed, the ylidene form was rejected. In reality, a small amount of this form is produced,[68] but the observation of the corresponding small splitting apparently requires a more sensitive apparatus. Nevertheless, the possibilities of the above method are very great because, by virtue of the weak dependence of $J_{^{15}N-H}$ on the structure, in most cases there is no need to synthesis model compounds. The magnitude of the splitting for the tautomer (B) is close to 90 Hz, while for the enolic form it is apparently zero,[69] which ensures the quantitative estimation of K_T.

New possibilities arise in connection with the use of high-field instruments and special pulse trains (INEPT) for increasing the sensitivity and the measurement of ^{15}N NMR spectra on the basis of the natural abundance of the isotope. The possibilities of the broad-band version of the INEPT procedure for the measurement of $J_{^{15}N-H}$ have been demonstrated recently in the study of the tautomeric acylmethylazines of the pyridine, pyrimidine, and quinoline series.[70]

In contrast to earlier data,[64,72] Cassity et al.[71] state that the equilibrium (A) ⇄ (B) occurs for a series of picolinylketones (XVIIa, d, f, g). It may be that[57] this claim is a result of the careless reading of the communication[67] to which the authors refer in order to confirm their conclusions. The contradictory nature of the data on the structures of simple acylmethylazines was pointed out as early as 1982 in a study[57] of the tautomeric equilibrium of t-butyl 2-picolinyl ketone (XVIIg) and its quinoline analogue in 25 solvents. The value of the above study[57] is somewhat reduced because the position of the "fast" equilibrium (B) ⇄ (C) was not investigated and it was assumed (referring to the study of Mondelli and Merlini[67]) that only the (A) ⇄ (C) equilibrium obtains for the pyridine analogue and only the (A) ⇄ (B) equilibrium obtains for the quinoline analogue. This approach can lead to inaccurate conclusions. Thus the examination of the spectral characteristics of acylmethylazines in various solvents has shown[73] that the third tautomer occurs also for the above ketones.

The tautomerism of 2-cyanoacetonylpyridine (XVIII) has been discussed.[74] On the basis of ^1H NMR, IR, and UV spectroscopic data, the authors[74] postulate that the enolic tautomer (C) predominates in chloroform, cyclohexane, and basic aqueous media, while the tautomer (B) predominates in methanol and in acid media.

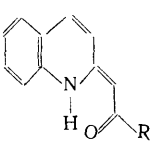


(C) ⇄ (B); (XX)

(XVIII): R = H; (XIX): R = $OCOCH_3$.

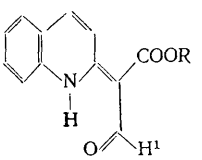
More reliable data, obtained by the joint application of the ^{17}O and ^{14}N NMR methods[75] showed that the equilibrium (B) ⇄ (C) occurs in $CHCl_3$ with the ylidene form predominating. A shift of the equilibrium towards the ylidene tautomer may be expected also for substituted cyanoacetonylpyridine (XIX), although the authors[76] give preference to the other chelate form (C). The ylidene structure of compound (XIX) is supported by the identity of the UV spectrum of compound (XIX) with that of its close analogue (XX), for which the formation of an enolic form of type (C) is uncharacteristic owing to the low tendency of the ester group to enolise. The significant difference between the chemical shifts of the chelate proton for compounds (XIX) and (XX) (δ = 17 and 14 p.p.m.), observed by Stein et al.,[76] may be caused by the difference between the strengths of the hydrogen bonds in the ylidene forms of these compounds.

Contradictory data on the structures of condensed acylmethylazines have been quoted in the literature. Thus the enolic structure has been attributed[77] to phenacylquinoline (XXI) and to acetonylquinoline (XXII). However, other workers[67] have adduced evidence in support of the ylidene form, in agreement with the data of Yamazaki et al.[78] Nevertheless, in the assignment of the signals in the ^1H NMR spectra of 2-phenacylquinoline (XXI), Hay and Wolfe[79] used the enolic form as a basis.



(XXI): R = C_6H_5;
(XXII): R = CH_3.

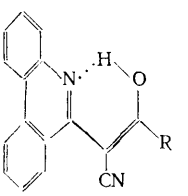
(XXI), (XXII)



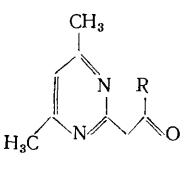
(XXIII)

In view of the absence of the characteristic splitting of the signals due to the protons of the methyl and methylene groups and also as a result of comparing the UV spectra of acetonylcholines and model compounds, it has been concluded[67] that the two forms (A) and (B) of 2-acetonylquinoline (XXII) are in equilibrium. The study of a series of acylmethylquinolines and of the formyl derivative (XXIII)[78,80] led to the preference being given to form (B) among the chelate tautomers. The conclusion that the formyl(quinolinyl)acetic ester (XXIII) has the ylidene structure can be reached in view of the absence of spin–spin coupling of $H^{(1)}$ and the proton of the hydroxy-group, which would have occurred in the case of the enolic tautomer.[80]

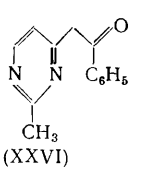
The structure of the phenanthridine derivatives (XXIV, R = CH_3, C_6H_5) has been examined in a study[81] where preference was given to the enolic form on the basis of the proton chemical shift (16.8 p.p.m.). This conclusion is inconsistent with the usually observed effect of the electron-accepting substituent and of annelation (in both cases the ylidene tautomer is stabilised) and requires additional confirmation.



(XXIV)



(XXV)

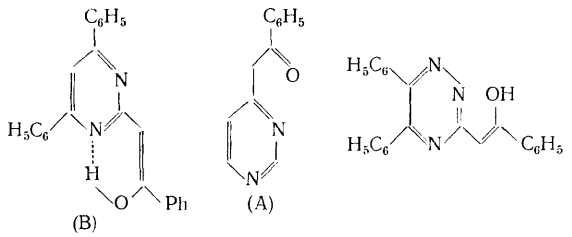


(XXVI)

In the series of diazines, studies have been made of the tautomerism of substituted acetonylpyrimidines (XXV) and phenacylpyrimidines (XXVI)[82–84] and also of 2- and 4-trichloro- and 2- and 4-trifluoro-acetonylpyrimidines.[85]

On the basis of ^1H NMR spectroscopic data for compounds (XXV) and (XXVI), it has been stated[82,84] that the tautomers (A) and (B) or (C) are present in the mixture, but the choice between the enolic and ylidene tautomer was not made. The tautomerism of

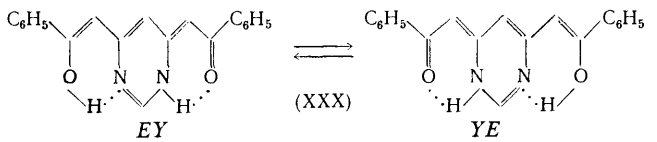
2-phenacyl-4,6-diphenylpyrimidine (XXVII) has been investigated by ^{1}H NMR and UV spectroscopy.[83] The absorption in the UV spectrum of the tautomeric forms (A), (B), and (C) was modelled by the absorption of the corresponding *C*, *O*-, and *N*-methyl derivatives. The absence of the ylidene tautomer (B) from the equilibrium was demonstrated; the ratio of the forms (A) and (C) is 1:2 (in $CHCl_3$) according to ^{1}H NMR data.[83]



(B) (XXVII) (A) (XXVIII) (XXIX)

Judging from the ^{14}N and ^{17}O NMR data, 4-phenacylpyrimidine (XXVIII) contains comparable amounts of the tautomers (B) and (C) [from ^{1}H NMR data, the fraction of form (A) in $CHCl_3$ is 20%].[86] The synthesis of a series of substituted acylmethylated pyrimidines, quinazolines, and pyrazines has been described,[87] but the tautomerism of these compounds has not been studied. The occurrence of the keto–enol equilibrium has been noted for phenacyl-1,3,5-triazine (XXIX) (with reference to ^{1}H NMR data).[42] However, these results do not permit a reliable exclusion of the presence of the ylidene tautomer.

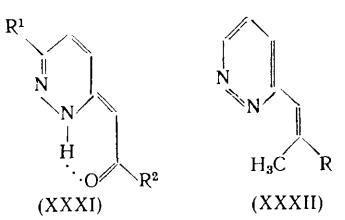
The tautomerism of 4,6-diphenacylpyrimidine (XXX) is more complex.[15] Using ^{17}O NMR and by observing the tautomerisation dynamics using ^{1}H NMR in $CHCl_3$, it has been possible to establish the presence of five tautomers (*KK*, *KE*, *KY*, *EE*, and *EY*, where *K*, *E*, and *Y* are indices denoting the keto-, enol-, and ylidene fragments in the 4- and 6-positions).



EY (XXX) *YE*

It is of interest to note that the [1,5]–[1,5]disigmatropic EY ⇄ YE equilibrium is an example of tautomerism of the cyclodismutation type, previously deduced within the framework of the formal classification of tautomeric systems.[11]

Among the chelate forms of acylmethylpyridazines (XXXI), preference has been given[88] to the NH form. The main evidence in support of this was obtained by comparing the ^{1}H NMR spectra in $CDCl_3$ with the spectra of model compounds (XXXII) (relative to the enolic form).

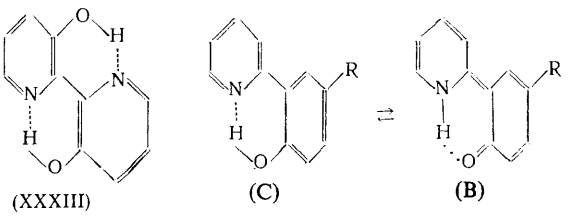


(XXXI) (XXXII)

However, the OH group in compound (XXXI) would be a stronger donor than the CH_3 group in compound (XXXII) as a result of which models of the type (XXXII) may prove to be relatively unsuitable. In particular, reliable ^{14}N and ^{17}O NMR data for phenacylpyridazine, which was considered by Ohsawa et al.,[88] have shown that the contents of the two chelate tautomers in $CHCl_3$ are comparable.[86]

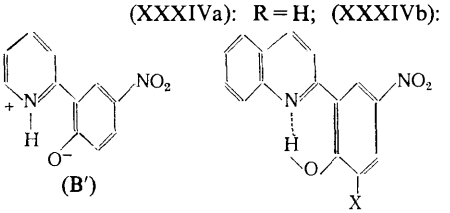
o-Hydroxyphenylazines and their condensed analogues are an interesting group of compounds capable of undergoing intrachelate tautomerism of the [1,5]sigmatropic type. The photoinduced tautomerisation of these compounds has been studied in detail in the series of *o*-hydroxyphenyl- and hydroxynaphthyl-azines,[89] including the procedure using laser flash photolysis with picosecond resolution.[90–92] Disigmatropic [1,5]–[1,5]tautomerisation has been observed for the bipyridyl analogue (XXXIII).[93] *o*-Hydroxyphenylazines are effective photostabilisers of polymers[94,95] and the characteristic features of their tautomerisation can have a significant effect on their properties. The tautomerism of these compounds in the ground state is therefore of special interest. In particular, it is of interest to discover the structural limits of the stability of the aromatic tautomeric form (to which total stabilising properties are attributed) as well as factors favouring the formation of the ylidene tautomeric form.

The first hypotheses concerning the occurrence of the ylidene form (B) were put forward as early as 1918 in a study of *o*-hydroxyphenylpyridine (XXXIVa).[20] Later it was suggested,[96] from IR spectra, that the *p*-nitrophenyl derivative (XXXIVb) has the zwitterionic structure (which is easily seen to constitute another resonance representation of the ylidene tautomer).



(XXXIII) (C) (B)

(XXXIVa): R = H; (XXXIVb): R = NO_2.



(B′) (XXXIVb)

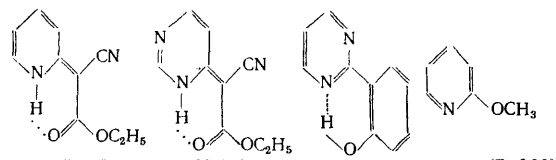
(XXXVa): X = H
(XXXVb): X = NO_2.

It has been shown with the aid of ^{17}O NMR and UV spectroscopic methods[97] that the ylidene tautomers of hydroxyphenylpyridine (XXXIVa) and of its nitro-analogue (XXXIVb) are not observed in $CHCl_3$. However, the ylidene tautomer of the nitrophenylquinoline (XXXVa) is present in small amounts while the content of this tautomer of the dinitro-derivative (XXXVb) becomes dominant.

The studies of the tautomerism of acylmethylazines examines above contain a large number of contradictory examples, sometimes involving mutually exclusive conclusions about the structures of the same compounds. This is caused primarily by the difficulties arising in the study of fast intrachelate equilibria by traditional methods. Reliable information about an intrachelate equilibrium of the type (B) ⇄ (C) can be obtained by observing the NMR spectra of the nitrogen and oxygen atoms which are involved directly in the tautomeric transformation. In contrast to the H and C atoms, the

hybridisation of the N and O atoms in the tautomeric transition changes, as a result of which the differences between the chemical shifts of the indicator nuclei should be extremely large (hundreds of p.p.m.).

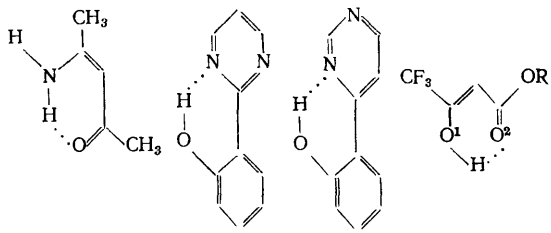
It has been suggested[68,86] that a combination of the ^{14}N and ^{17}O NMR methods be used to establish the position of the intrachelate tautomeric equilibrium of the type (B) ⇄ (C). The ratio of the (B) and (C) tautomers is estimated from the positions of the nitrogen and/or oxygen signals relative to the signals of model compounds. The corresponding azinylidenecyanoacetic esters were used to estimate the chemical shifts of the nitrogen atom in the ylidene form. The position of the ^{14}N NMR signal for the enolic forms was modelled with the aid of *o*-hydroxyphenylazines, for which the enolic structure of the chelate tautomer has been established reliably.[98]

Compound 

$\delta(^{14}N)$, p.p.m. -215 ± 5 -230 ± 3 -130 ± 5 -110 (Ref.99)

The ^{14}N NMR signal of the NH form (B) is fairly narrow ($\Delta_{1/2} \simeq 200$ Hz) in contrast to the signal of form (A) ($\Delta_{1/2}$ up to 800 Hz).[99] The ^{14}N NMR spectroscopy is therefore effective when the ylidene form predominates in the equilibrium (B) ⇄ (C).

2-Aminopent-2-enone, in which the carbonyl group is incorporated in the enaminocarbonyl fragment involved in the hydrogen bond, as in the ylidene form, was used to model the ^{17}O NMR shifts of the ylidene tautomer (B). In selecting a model for the ^{17}O NMR of the enolic tautomer (C), it was important to take into account the conjugation of the OH group with the heteroaromatic ring through the double bond and also the intramolecular hydrogen bonds. These requirements are satisfied in many respects by *o*-hydroxyphenylazines [$\delta(^{17}O) \simeq 94-97$ p.p.m.] and the enolic forms of β-ketoesters.[98] Comparison of the chemical shifts of hydroxyphenylazines and β-ketoester enols showed[98] the position of the OH signal of the unmodified enolic fragment depends comparatively little on the form of the proton-accepting component of the chelate ring (the carbonyl group in β-ketoazines and the azine fragments in *o*-hydroxyphenylzines).

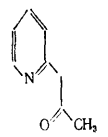
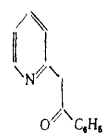
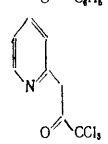
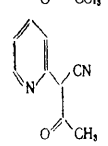
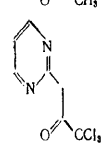
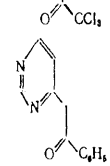
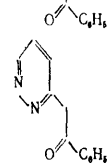
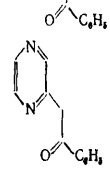
Compound 

$\delta(^{17}O)$, p.p.m. 419 96 94 O^1 96, O^2 315

The accuracy of the determination of the contents of the (B) and (C) tautomers by the ^{14}N and ^{17}O NMR methods has been analysed.[68]

The ^{14}N and ^{17}O NMR spectroscopic data in Table 1 agree fairly satisfactorily, which makes it possible to establish reliably the structure of acylmethylazines and to resolve the contradictions existing in the literature. Thus the chemical shifts found for acetonylpyridine and phenacylpyridine indicate the virtually complete displacement of the equilibrium (B) ⇄ (C) to the enolic tautomer (C). The ^{17}O NMR data, which are more accurate when the enolic tautomer predominates, show that, together with forms (A) and (C), the ylidene tautomer is also present albeit in small amounts. The accumulation of electron-accepting substituents in the exocyclic group favours the ylidene tautomer to a greater extent. Isotypical derivatives of azines exhibit different tendencies towards conversion into the ylidene tautomeric form (B), whose fraction in the intrachelate equilibrium (B) ⇄ (C) is a maximum for 4-pyrimidine and 3-pyridazine derivatives. The high sensitivity of the intrachelate tautomeric equilibrium to the effect of the

Table 1. The chemical shifts in the ^{14}N and ^{17}O NMR spectra of acylmethylazines and the ratios of the tautomers (B) and (C).[86]

Compound	$\delta(^{14}N)$, p.p.m.	Tautomer ratio (C)/(B)	$\delta(^{17}O)$, p.p.m.	Tautomer ratio (C)/(B)
	-130 ± 5	>90/10	143 ± 3	>90/10
	-131 ± 5	>90/10	125 ± 3	>90/10
	-194 ± 3	25/75		
	-199 ± 1	20/80	356 ± 1	10/90
	-140 ± 5	90/10	162 ± 3	80/20
	-142 ± 5	90/10	162	80/20
	-131 ± 5	50/50		
			109 [100]	100/0

substituent at the carbonyl group is striking. Thus transition from acetonylpyridine (XVIIa) to its trichloromethyl analogue reverses the ratio of forms (B) and (C).

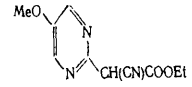
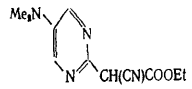
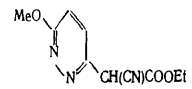
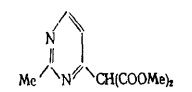
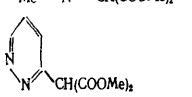
^{14}N and ^{17}O NMR methods have been used to investigate the tautomerism of acylmethylpyrazines and their annelated analogues.[100] Compared with pyridine derivatives, acylmethylpyrazines exhibit a smaller tendency towards transition to the ylidene form, which remains unstable even in the case of trifluoroacetonylpyrazine. As for other acylmethylazines, annelation greatly stabilises the NH tautomer

The above data demonstrate the great potential possibilities for the joint employment of the $^{15,14}N$ and ^{17}O NMR methods in the study of the tautomerism of heterocyclic compounds.

IV. Thermodynamics, kinetics, and mechanism of the tautomeric interconversions of azinylmethanes

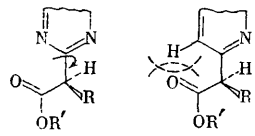
The temperature dependence of the equilibrium and the thermodynamic parameters ΔH and ΔS for pyrimidine and pyridazine derivatives[101] are listed in Table 2. The tautomeric equilibrium (A) ⇄ (B) proved extremely sensitive to changes in temperature. An extremely high ΔS has been observed for compounds (VIIIb, c), which is uncharacteristic of prototropic equilibria as a whole. For example, ΔS for the keto–enol equilibria involving benzoylacetic esters or for the tautomerism of 2-hydroxypyridine varies in the range from 8 to 16 J mol^{-1} K^{-1}.[102,103] The values of 60–70 J mol^{-1} K^{-1} found by Petrenko et al.[101] agree with the entropies in the azido-tetrazole tautomeric equilibrium,[101,104] which, however, is not of the prototropic type.

Table 2. Thermodynamic parameters of the tautomeric equilibrium.[101]

Compound	Structural formula	ΔH, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}
(VIIIb)		21.1±0.2	62±1
(VIIIc)		23.2±0.2	71±1
(XXXVI)		7.9±0.6	47±2
(XXXVII)		12.2±0.6	38±2
(XXXVIII)		4.7±0.8	24±2.5

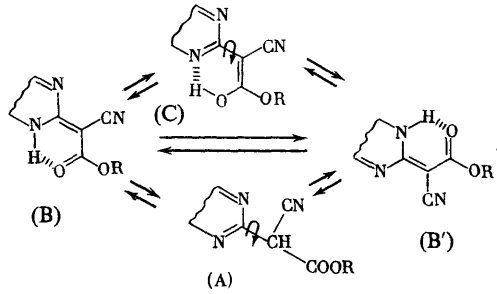
The unfavourable entropy change on transition to the ylidene tautomer in the case of pyrimidinylcyanoacetic esters (VIIIb, c) is evidently associated with the loss of freedom of rotation about the exocyclic C–C bond in the ylidene tautomer.

Scheme 2



When the C–H fragment, which is more bulky than the N atom, is present in the β-position [compound (XXXVI), Table 2], the rotation in the tautomer (A) becomes hindered (Scheme 2), which reduces the difference between the entropies of the tautomers (A) and (B).[105] The further decrease in ΔS for the malonic esters (XXXVII) and (XXXVIII) (Table 2) is associated with still greater hindrance to the rotation of the more bulky exocyclic group.[101]

The kinetic characteristics of the tautomeric transformations of azinylmethanes were obtained in a study of the tautomerism of pyrimidinyl- and pyridazinyl-malonic esters[50] as well as phenylacylquinolines.[106] In both studies, it was concluded that the tautomerisation mechanism is of the ionic-dissociative type and is close to that which is well known for keto–enol tautomeric systems. This mechanism is supported by the following experimental data: the occurrence of acid–base catalysis, the dependence of the rate of tautomerisation on the concentration of the tautomeric compound (autocatalysis), and the ready deuterium exchange of the acid protons of the NH and CH groups.[106,107] In the ionic-dissociative mechanism, the dissociation (or formation) of a C–H bond is the rate-limiting stage; this has been confirmed in a study[107] of the tautomeric equilibrium involving pyrimidinylcyanoacetic ester (VIIIb) by the kinetic isotope effect (k_H/k_D = 3.5).

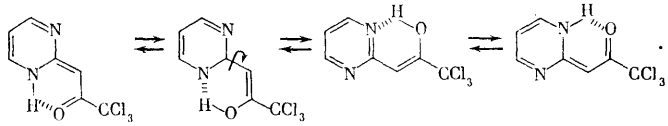


The mechanism of the annular tautomerism of the type (B) ⇄ (B′) has been studied.[38,39] The merging of the signals of the methoxy-groups in the ^1H NMR spectrum of 4,6-dimethoxy-1,3,5-triazinyl-2-cyanoacetic ester (IX) was observed on passing from $CDCl_3$ to DMSO and dimethylformamide (DMF)[39] and the authors suggest that this merging is caused by a rapid intramolecular reaction proceeding via the intermediate enolic form. However, later UV spectroscopic data[38] obtained in various solvents indicate a pronounced (if not complete) ionisation of compound (IX) in DMSO and DMF. Thus the changes observed in the ^1H NMR spectrum[39] can be altogether unrelated to tautomerism. The mechanism of the annular tautomerism has been investigated[38] in relation to the pyrimidinyl-2-cyanoacetic ester (VIIIa), which is less acid and is scarcely ionised in DMSO or DMF.

Evidently the [1,3]sigmatropic tautomerisation examined above can involve with equal probability both the N(1)H and the N(3)H group. Hence it follows that, in the presence of even traces of form

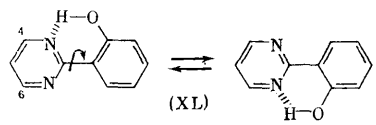
(A), the interconversion of forms (B) and (B′) via the tautomer (A) is one of the routes of [1,5]tautomerisation. The mechanism with participation of the aromatic tautomer (A) should differ from the other possible mechanisms of the (B) ⇄ (B′) process (for example, via the formation of the enolic form of the anion) by the presence of a kinetic isotope effect, which has in fact been detected[38] in the study of the kinetics of the degenerate tautomeric transformation of compound (VIIIa) with the aid of the pulse version of the method involving the transfer of a magnetic saturation label.[108] It is believed that the mechanism with participation of form (A) is not ruled out also in the case of the triazinylcyanoacetic ester (IX) mentioned above, particularly bearing in mind that appreciable amounts of the aromatic tautomer of this compound in hexane have been detected.[38]

Evidently the probability of an intramolecular mechanism of the tautomeric type (B) ⇄ (B′) transformation via the enolic tautomer increases if the side group contains the readily enolisable carbonyl group. Such a mechanism apparently actually operates for 2-trichloroacetonylpyrimidine (XXXIX):[86]



(B) (C) (C′) (B′)

Although comparable amounts of the ylidene form are present in the equilibrium with the enolic form of compound (XXXIX),[86] the C(4) and C(6) signals in the ^{13}C NMR spectrum have been averaged as a consequence of the rapid (B) ⇄ (B′) exchange even at room temperature. Since the (B) ⇄ (C) stage is extremely fast,[60,61] the following question arises: can the barrier to the rotation in the enolic form, associated with the rupture of a fairly strong hydrogen bond, be so low that averaging at this temperature is ensured? The study of the temperature spectra of the model compound (XL) showed that this type of rotation does indeed have a low barrier. Thus the separation of the C(4) and C(6) signals in the ^{13}C NMR spectrum arises only when the solution of compound (XL) in $CHCl_3$ is cooled to −50 to −60 °C.[86]



(XL)

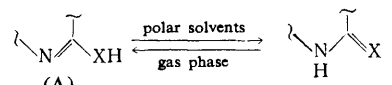
Thus the mechanism of the degenerate tautomeric transformation (B) ⇄ (B′) for substituted azinylmethanes can change depending on the nature of the substituents in the side group.

V. The influence of the solvent and structural factors on the tautomerism of azinylmethanes and general characteristics of tautomeric equilibria of the azinyl–azinylidene type

1. The influence of the solvent

Vigorous studies in recent years have shown that the solvent can have a decisive effect on tautomeric equilibria of the azinyl–azinylidene type. The change to solvents of low polarity and the gas phase greatly destabilises the ylidene form, which has been repeatedly demonstrated for hydroxyazines.[109–110] The existence of reliable experimental data made compounds of this series a favourite model for testing the most modern computational schemes for medium effects based on quantum-chemical calculations and the Monte Carlo method.[111,112]

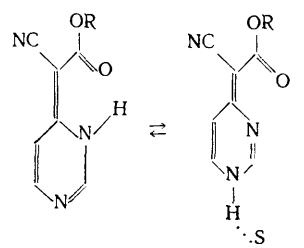
Theoretical estimation of the effect of solvent polarity for azinylmethane derivatives[113] within the framework of the method of solvatons[114] permitted the elucidation of the principal trend: a non-polar solvent and the gas phase favour the aromatic form (A), while a polar solvent shifts the equilibrium towards the ylidene tautomer (B):



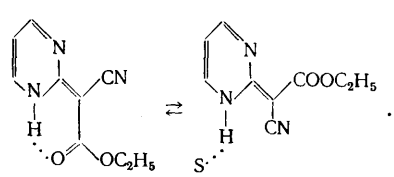
(A) (B)

X = O, NR, CR^1R^2.

Numerous experimental data obtained in the study of the tautomeric equilibria of azinylmethanes in various solvents agree well with this prediction.[113] This behaviour is apparently associated with the specific rearrangement of the electronic structure of the heterocycle on passing to the ylidene form. Judging from quantum-chemical calculations,[113] a marked alternation of the electron density in the ring is characteristic of this form, which, on the basis of the Born approximation,[115] favours solvation by polar solvents. It has been suggested[113] that bulky substituents at a CH fragment, which do not undergo changes in structure on tautomerisation, can abolish the tendency mentioned above. It may be that the low sensitivity of the tautomerism of derivatives of malonic and dinitrophenylacetic esters to the character of the solvent is in fact associated with this factor.[113]



In many cases the change of solvent induces the appearance of a new tautomeric form. This situation is characteristic of derivatives of 4-pyrimidinylmethane, for which the use of polar or specifically solvating solvents leads to the appearance of the ylidene tautomer with the *para*-quinonoid disposition of the double bonds.[35–37] Judging from quantum-chemical calculations[36] and experimental data,[116] this feature is characteristic also of other 4-substituted pyrimidines, for example 4-hydroxypyrimidines.[116] On the other hand, in the case of 2-pyrimidinylcyanoacetic ester (VIIIa), the addition of a highly basic solvent (DMSO, HMPA) apparently leads to the dissociation of the intramolecular hydrogen bond and the appearance of non-chelate tautomers of the ylidene type:[117]

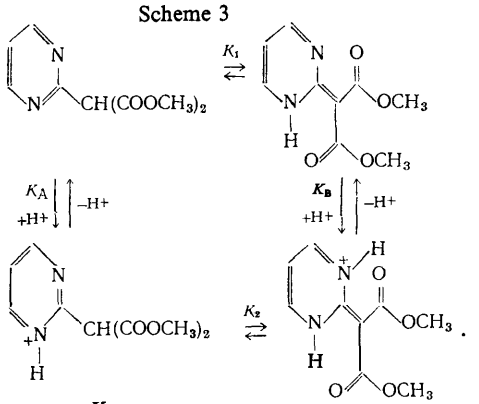


(VIII a)

For highly acidic compounds [for example, 2-trifluoromethyl-4-pyrimidinylcyanoacetic ester (VIIc)], dissolution in DMSO (or HMPA) is accompanied by appreciable and sometimes even complete ionisation.[37] This can be readily established by comparing the UV spectrum of this compound in DMSO with the spectrum of the corresponding sodium salt. Nevertheless, the possibility of ionisation in solutions is frequently not taken into account, which can lead to erroneous conclusions.[38,39] Hydroxylated solvents (alcohols, acetic acid) stabilise the ylidene tautomer both as a result of solvent polarity and as a result of specific solvation.[113]

The effect of protonated solvents (CF_3COOH), which has been investigated in relation to azinylmalonic and azinylcyanoacetic esters,[117,118] is very strong. It has been suggested[117] that, by virtue of the conjugation of the C=N fragment with the electron-donating NH group, form (B) is apparently more basic ($K_B > K_A$). According to Eqn. (1), this means that protonation shifts the tautomeric equilibrium towards the ylidene form. The most striking example is provided by the equilibrium of derivatives of 2-pyrimidinylmalonic esters,[117] which exist in form (A) and do not exhibit tautomeric properties in neutral solvents of the type of $CHCl_3$. On the other hand, in the presence of trifluoroacetic acid, whose acidity ensures the monoprotonation of pyrimidine derivatives, the equilibrium shifts towards the ylidene tautomeric form (B).[117]

Scheme 3



$$K_2 = K_1 \frac{K_B}{K_A} \qquad (1)$$

The reverse shift—towards the protonated form (A)—is observed under these conditions for pyridyl- and quinolinyl-cyanoacetic esters, which has been confirmed by UV and NMR spectroscopic data.[30,118]

The high sensitivity of the tautomeric equilibrium to solvation effects is characteristic also of the intrachelate tautomerism of the [1,5]sigmatropic type. It has been found for *o*-hydroxyphenylazines[97] and acylmethylazines[73,100] that, as in the case of tautomeric equilibria of the [1,3]sigmatropic type, polar solvents stabilise the ylidene form.

Comparison of the results presented above the effect of the solvent on the tautomerism of azinylmethanes with data on the tautomerism of hydroxy- and amino-azines[3] suggests that prototropic equilibria of the azinyl-azinylidene type as a rule obey a universal rule: a decrease in solvent polarity or transition to the gas phase destabilises the tautomer of the ylidene type. On the other hand, if account is taken also of data for the effect of the solvent on non-prototropic equilibria of the azinyl—azinylidene type (for example, the tautomerism of azidoazines where polar solvents favour the tautomer of the ylidene type—the tetrazole form[119]), then the above tendency is seen to be very general for the entire family of tautomeric equilibria of the azinyl—azinyldene type. There is no doubt that such generality is caused by the similarity of the topologies of the bonds of the corresponding tautomers (see Scheme 1) [Scheme 3?], which is independent of the type of substituent.

2. The influence of structural factors on the tautomeric equilibrium

The combination of a large number of different tautomeric systems into the family of tautomeric equilibria of the azinyl—azinylidene type[86] is not purely formal. Although the type of exocyclic fragment introduces its characteristic features, nevertheless it is clear that the topological similarity in the (A) ⇄ (B) bond rearrangement predetermines the existence of certain general features of the tautomerism of the azaheteroaryl—azaheteroarylidene type. This follows from the profound relation between the topology of the molecules and their electronic structure, which has been discovered in recent years.[120] Bearing in mind the importance of tautomerism of the azinyl—azinylidene type and the existence of extensive experimental data, the search for such features is of very great current interest. Evidently the dynamic characteristics of the tautomerism (mechanism, kinetics) will vary markedly as a function of the type of the azine component and the nature of the exocyclic fragment. On the other hand, general features may be expected primarily as regards the thermodynamic characteristics and their dependence on various factors. The medium effects, the characteristics of the influence of which were examined above, and the effects of structural changes must be regarded as the most important factors. Among the latter, one can differentiate the influence of the type of heterocyclic nucleus and of the substituents in the heterocycle and in the side fragment as well as the influence of annelation.

Despite the extensive experimental data on the tautomerism of substituted azines, the number of systematic data concerning the effect of structural factors is small. Since such studies are extremely laborious, the following approach to the study of the effect of structural factors is useful:[86,121–124] for a topologically similar group of tautomeric systems, the electronic structures of the tautomers (the redistribution of charges and bond orders in the tautomeric transition and the change in frontal orbitals) are analysed. Using the formalism of the molecular orbital perturbation method (MOP), the principal trends and the characteristic features of the effect of structural factors on the position of the tautomeric equilibrium can be discovered. Taking into account the resulting prediction, a specific experimental test is carried out in order to formulate finally the manifested features or trends.

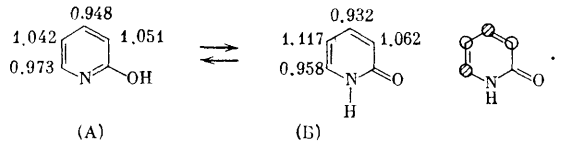
Examination of the frontal MO of the tautomers in the series of hydroxy-, amino-, and methyl-azines[122] made it possible to note the isolobal analogy[125] for isotypical tautomers: the forms and energies of the corresponding frontal MO are similar. Since the interaction of substituents with isolobal fragments is qualitatively similar, one may expect similar trends in the "response" of various equilibria of the type (A) ⇄ (B) to identical structural perturbations.

The effects of the heteroatom and the substituent can be estimated conveniently qualitatively with the aid of "difference charts", which reflect the relative changes in key electronic, energy, or orbital characteristics in the transition (A) ⇄ (B). Employing the usual approximations of the MOP method, it has been found that,[86,121–124] in order to estimate the effect of the heteroatom and the inductive and mesomeric effects of the substituents, it is

necessary to use the charts of the differences between the charges, energies, and the squares of the coefficients of the frontal MO. Although the calculations which have been performed correspond to the gas phase, allowance for the polarity of the medium within the framework of the Germer model[114] demonstrated the low sensitivity of the difference charts to the solvent.[122–124]

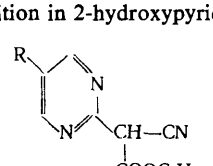
In the analysis of the inductive effect of the substituent within the framework of the MOP method, one considers the change in the π-electron density on the atom at which the substituent is introduced.[126] According to non-empirical calculations (using the STO-3G basis set),[123] the transition from form (A) to form (B) in the case of 2-hydroxypyridine leads to an increase of the π-electron density in the 3- and 5-positions and to its decrease in the 4- and 6-positions in the heterocycle. These changes are presented in Scheme 4 as graphical difference charts on which the shaded positions correspond to a positive sign of Δq and the open positions correspond to a negative sign.

Scheme 4

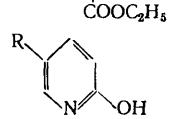


Accordingly, the fraction of the tautomer (A) should increase following the introduction of an electron-accepting substituent in the shaded positions in the heterocycle or of an electron-donating substituent in the unshaded positions. This prediction has been largely confirmed experimentally for substitution in the α-position (relative to the heteroatom), where electron-accepting inductive substituents stabilise form (A), while electron-donating substituents destabilise it.[3,122] The trifluoromethyl group has precisely this effect on the equilibrium in the series of substituted hydroxy- and methyl-azines.[3,123] Nevertheless, the effect of substituents does not reduce to electron-donating substituents favouring the pyridine form and electron-accepting substituents favouring the aromatic form. For example, the introduction of the methyl group in the 5-position in 2-pyrimidinylcyanoacetic ester (VIIIa) leads to a shift of the tautomeric equilibrium towards the aromatic tautomer, as predicted by the charge difference charts.[123]

Comparison of the charge difference charts[123] shows that their topology for mono- and di-azines remains constant regardless of the type of exocyclic tautomerising fragment and the nature of the heterocycle. One may therefore expect that the character of the *I* effect of substituents in the series of tautomeric equilibria of the azinyl–azinylidene type is to a significant extent universal. Indeed, according to the available experimental data,[123] the effect of the methyl group on the tautomerism of 2-hydroxypyridine is similar to its effect on the position of the tautomeric equilibrium involving pyrimidinylmethanes: the introduction of the methyl group in the 5-position in 2-hydroxypyridine stabilises the aromatic tautomer.



R	K_T (hexane)
H	0.67
CH_3	3.6



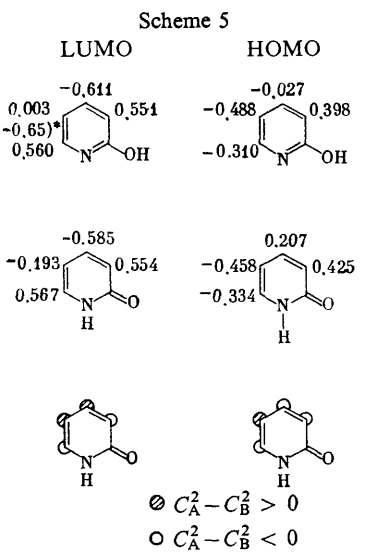
R	pK_T (water)
H	3.0
CH_3	2.6

$K_T = [A]/[B]$

Ultimately, comparison of the charge difference charts with the experimental data made it possible[123] to formulate the main trend in the inductive effect of substituents—the introduction of electron-donating substituents in the *meta*-position relative to the exocyclic tautomerising fragment shifts the equilibrium towards the ylidene form, while its introduction in the *ortho*- and *para*-positions shifts the equilibrium towards the aromatic tautomer. Electron-accepting substituents have the opposite inductive effect.[123]

It is of interest that, for substituents of the mesomeric type, such reversal of the effect on transition from electron-donating to electron-accepting substituents may not in fact be observed, which can be seen from a comparison of the charts for the difference between the squares of the coefficients of the frontier MO (Scheme 5). Thus the introduction of mesomeric substituents of both electron-donating and electron-accepting types in the *para*-position relative to the tautomerising fragment should shift the equilibrium towards the aromatic tautomer because for this position the difference between the squares of the coefficients of both frontier MO is greater in form (A) than in form (B).

Scheme 5



*Coefficient of a neighbouring unoccupied MO

Experimental data agree with this conclusion. For example, the introduction of the electron-donating $N(CH_3)_2$ group, the electron-accepting p-$NO_2C_6H_4$ group, and the "neutral" C_6H_5 group in the 5-position of 2-pyrimidinylcyanoacetic ester (VIIIa) increases the fraction of the aromatic tautomer (Table 3). A similar behaviour

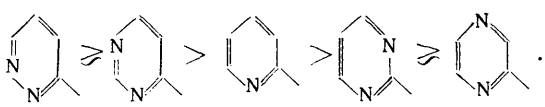
Table 3. Tautomeric equilibrium constants for 5-substituted 2-pyrimidinylcyanoacetic esters (VIII).[122]

R	K_T(A/B)	
	$CDCl_3$	hexane + 2% $CHCl_3$
H	0.01	0.67±0.02
OCH_3	0.54	3.0±0.05
$N(CH_3)_2$	0.66	
C_6H_5	0.01	1.0±0.05
$O_2NC_6H_4$	0.25	

has been observed also for cyanoacetic esters of the pyridazine series[127] and also for hydroxy-azines, which has been noted by Petrenko and Lapachev.[122] The latter implies that, in the case of mesomeric substituents, the character of the effect of the substituent in azines with different exocyclic tautomerising fragments is the same.[122]

It follows from the charts of the differences between the squares of the coefficients[122] and the π-electron densities[123] that identical effects of the substituent (as a result of the mesomeric and inductive contributions) on the position of the tautomeric equilibrium should be encountered fairly rarely. Bearing in mind the character of the approximations of the simple MOP method, direct comparison of the contributions of the inductive and mesomeric effects on the basis of difference charts is scarcely possible. At the same time, joint examination of the experimental data and difference charts frequently makes it possible to discover which effect predominates.[122]

In order to understand and predict the tautomeric properties in the series of different azines, it is important to estimate the tendency of each type of azine to rearrange to the ylidene form. Analysis using difference charts and experimental tests have shown[124] that isotypical azine derivatives are fairly clearly differentiated as regards their tendency to undergo a transition to the ylidene tautomeric form. Thus it has been shown that the transition from the pyridine tautomeric compound to the analogous 2-pyrimidine or 2-pyrazine derivative promotes a shift of tautomeric equilibrium towards the aromatic tautomer, while transitions to 4-pyrimidine and 3-pyridazine derivatives promote the transition to the ylidene tautomer.[124] Thus the series of relative tendencies by isotypical azine compounds to undergo a transition to the ylidene tautomeric form is as follows:



Analysis of the distribution of electron density on the nitrogen atoms and in the bonds, the search for isolobal analogy, and inspection of difference charts for tautomeric pairs have made it possible to discover the basis of this similarity, which is observed among tautomeric equilibria of the azinyl–azinylidene type. Despite the multiplicity of approximations, which make it necessary to treat with caution the predictions obtained, the simplicity and clarity of the method make it promising for the construction of a general approach to the study of equilibria of the azinyl–azinylidene type and also of other types of tautomeric equilibria differentiated on the grounds of their topological relationship.

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The data examined show that tautomeric interconversions occur very widely in the series of substituted azinylmethanes. Apart from their independent importance, tautomeric azinylmethanes are very convenient models for the determination of the general characteristics of the tautomerism of the azinyl–azinylidene type, which is the most important type of tautomerism in the series of azines.

The MOP method proved to be effective for the discovery and prediction of features of this kind. Its use makes it possible to examine from a general standpoint the dependence of the tautomeric equilibrium of the azinyl–azinylidene type on structural factors. A similar methodology (the differentiation of a family of tautomeric equilibria on the basis of topological criteria, analysis of the similarity of the electronic structures of the tautomers, the use of the MOP method for the interpretation of experimental data, and the prediction and determination of the characteristic features) can be applied also to other classes of tautomeric equilibria.

Tautomeric azinylmethanes constitute one of the examples of molecules with a similar behaviour, which exist in different forms depending on the structure, medium, temperature, or irradiation. There is no doubt that interest in "flexible" molecules of this kind with extensive structural possibilities will continue to grow in the future, especially in connection with the construction of biochemically important molecules and their analogues, as well as compounds with more complex functions for applied purposes. The experience gained in the study of the tautomerism of heterocycles will then also prove essential.

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Neutral acyclic analogues of crown-ethers and cryptands and their complex-forming properties

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ABSTRACT. **The review deals with neutral podands (acrylic analogues of crown ethers) of various types, their structures, their complex-forming properties, and their practical applications. Phosphorus-containing and analogous organoelement podands are not included in the review.**

The bibliography incorporates 241 references.

Contents

I.	Introduction	283
II.	Neutral acyclic unbranched ligands — monodands	283
III.	Oligo(poly)podands	289
IV.	Applications of neutral acyclic complex-forming agents	292

I. Introduction

The term "podands" appeared in the chemical literature comparatively recently — towards the end of the 1970s.[1,2] It embraces various types of acyclic polyether complex-forming agents. The name comes from the Greek word "podos" — foot. In the podand molecule, there is one or several "feet" formed by polyether chains with various end groups. According to the number of such feet, podands are divided into mono-, di-, tri-, and poly-podands. Compounds of this type can be investigated long before the appearance of the term "podands" itself. Thus the simplest representatives of monopodands [diethyl ethers of oligo(ethylene glycols — glymes] became well known in the 1950s–1960s as solvents solvating alkali and certain other metal cations.[3,4] Polyether acyclic antibiotics (nigericin, monensin, etc.), containing tetrahydrofuran and tetrahydropyran rings in the chain, which were discovered and vigorously investigated in the 1950s–1970s, belong to the same type of complex-forming agents.[5] These compounds effect the transport of alkali metals through artificial and biological membranes. In the complex formation reaction, the molecules of acyclic antibiotics twist round a cation and form a pseudoring stabilised by the intramolecular interaction of the end groups.

The specific synthesis of podands as a special class of ligands began to develop mainly after Pedersen's discovery in 1967 of the complex-forming properties of crown ethers.[6] Oligo- and poly-(ethylene glycols) and glymes began to be regarded as open-chain analogues of crown ethers. Polydentate acyclic complex-forming agents of a new type were created on their basis[1] and found extensive application as solvents. Despite certain advances, this field nevertheless remained of secondary importance compared with the much more thoroughly developed and popular field of macrocyclic complex-forming agents.[7,8] However, in recent years open-chain analogues of crown-ethers have attracted increasing attention because of their availability, fairly high effectiveness, and the possibility of regulating on a wide scale their complex-forming properties by altering their structure. Their properties as phase-transfer catalysts,[9–12] extractants,[13,14] and as components of ion-selective electrodes[15] are being investigated. The growing interest in this new class of complex-forming agents is reflected by review articles[1,16,17] on this topic.

The present review differs from those already published by a much more complete coverage of literature (up to 1988), an attempt at the analysis of the dependence of the complex-forming capacity of podands on their structure, and a discussion of the applied aspects of the problem.

II. Neutral acyclic unbranched ligands — monopodands

1. Introduction

The specific solvation of alkali and alkaline earth metal cations by ethylene glycol ethers and their oligomers (glymes) is well known.[3,4] The use of these compounds as solvents for organic anionic reactions is in fact based on this phenomenon. Diglyme, which is in essence a fragment of the 18-crown-6 ether molecule, has come to be widely used. Following the discovery of crown-ethers in the second half of the 1960s, chemists again turn their attention to oligo(ethylene glycols) and glymes as cheaper analogues and began to investigate vigorously their complex-forming properties relative to those of crown-ethers.[18–21]

The principal method of synthesis of monopodands having the general formula $RO(CH_2CH_2O)_nR$ with various end groups is the Williamson reaction between the corresponding dihalides and hydroxyl-containing compounds in the presence of a base.[1]

Individual oligo- and poly-(ethylene-glycols) are obtained as a rule[22] by the reaction of the monoalkoxide of the lowest oligo-(ethylene glycol) with the dihalide of the corresponding oligo(ethylene glycol) using alkali metals or their hydroxides as metallating agents. The alkoxide of the lowest glycols was synthesised using sodium hydroxide, distilling away the water formed as a result of the reaction.[23] The yields of poly(ethylene glycols) do not then exceed 60%.

Ethers of oligo(poly)(ethylene glycol) were obtained by alkylating the corresponding alkali metal glycosides with a 1.5–3.0-fold excess of the alkyl halide at 50–90 °C in a solvent or in its absence. They

are freed from salts by filtration or with the aid of ion-exchange resins.[24]

The formation constants of the complexes of podands with metal cations are determined by NMR, IR, and UV spectroscopy, calorimetry, conductimetry, potentiometry, and extraction methods.

2. Oligo(poly)(ethylene glycols) and glymes

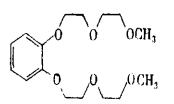
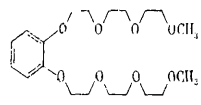
The formation of complexes by poly(ethylene glycols) (in which the number of units is $n = 1-8$) with alkaline and alkaline earth metal cations in aprotic solvents has been observed by the NMR method.[25] The formation constants of the complexes of glymes with alkali metal picrates in toluene were measured spectrophotometrically and were compared with data for crown-ethers.[26]

Oligo- and poly-(ethylene glycols) exhibit a fairly strong capacity for ion–dipole interaction with alkali and alkaline earth metal cations in methanol, which is a polar proton-donating solvent.[27–35] The interaction is in general determined by the ionic radius of the cation and the number of glycol units. The relatively strong interaction with large cations is due to the flexibility of the glycol molecule, which is able to assume the energetically favourable *trans*, *gauche*, *trans*-conformation.[36,37] The weak interaction with lithium and sodium cations has been explained[30] by the vigorous solvation of the latter by methanol. However, there exist conductimetric data[38] according to which glycols with $n = 2-4$ form fairly stable complexes with lithium picrate in isopropyl alcohol. Their composition corresponds to metal:ligand = 1:2 and their stability constants are approximately the same ($\lg K_{st} \simeq 2.37-2.51$). It has been shown[39] that in an aprotic solvent (toluene) the lower glycols with $n = 2-4$ are also capable of dissolving alkali and alkaline earth metal mono-, di- and tri-nitrophenoxides. According to NMR data,[28,40] the optimum number of units in the oligo(ethylene glycol) is six in the interaction with sodium and calcium cations, seven in the interaction with potassium, rubidium, caesium, and strontium cations, and five–seven for the barium cation. Glymes having the same number of binding sites as a rule interact somewhat more weakly with sodium and calcium cations in methanol, whereas the monomethyl ethers of the corresponding glycols occupy an intermediate position[28,32] (Table 1). On the other hand, it has been shown for a large series of poly(ethylene glycols) and their mono- and di-methyl ethers by the potentiometric method that,[31,32] with increase in the length of the polyether chain, the stability of the complexes of these ligands with the sodium cations increases (Table 1). Neither maxima, nor the attainment of a plateau, nor a decrease in complex-forming capacity were observed under these conditions. The complex formation constants for poly(ethylene glycols) and their derivatives with molecular weights in the range 1000–14000 ($n = 24-319$) are closer to those for 15-crown-5- and 18-crown-6-ethers. The stability of the sodium complexes on poly(ethylene glycols) and their ethers with a lower molecular weight is lower by 2–3 orders of magnitude than the stability of the complexes of the above macrocyclic compounds.[32,41] The replacement of two methyl end groups by the $C_2H_5OCOCH_2CH_2$ groups has little effect on the complex formation constants. The replacement of the central ethylene glycol unit by the rigid catechol unit is hardly reflected in the complex-forming properties of glymes[27,42] (Table 1). Poly(ethylene glycols) with a 1,2-acenaphthene fragment[43] and glymes with a central ferrocene nucleus[44] are known.

The stability constants of the lanthanide complexes of tetraglyme in propylene carbonate have been determined potentiometrically.[45] The stability of these complexes ($\lg K_{st} = 5.05$) proved to be lower by 1.5 orders of magnitude than in the case of 15-crown-5-ether and higher by an order of magnitude than for the complex of 3-t-butylbenzo-15-crown-5-ethyl.

Not only association with metal cations in solutions but also the formation of crystalline complexes is characteristic of oligo(ethylene glycols) and their dimethyl ethers. Numerous studies have been devoted to the synthesis and crystal structures of the complexes of glymes with transition metal salts.[1] According to the principles of hard and soft acids and bases, the most stable complexes are formed with transition metal cations by analogues of glymes with nitrogen or sulphur atoms or their combinations.[46–54] Crystalline complexes of oligo(ethylene glycols) and their derivatives with lanthanide nitrates and perchlorates have been obtained.[55,56]

Table 1. The logarithms of the stability constants of complexes of poly(ethylene glycol) ligands $R^1O(CH_2CH_2)_nR^2$, certain other ligands, and macrocycles with alkali metal halides in methanol.

n	R^1	R^2	$\lg K_{st}$			Refs.
			$Na^+(Cl^-)$	$K^+(I^-)$	$Cs^+(Cl^-)$	
4	H	H	1.64	—	—	[32]
4	CH_3	CH_3	1.28	1.72	1.45	[27]
4	CH_3	CH_3	1.44	1.59	1.43	[33]
5	H	H	—	2.01	1.29	[33]
5	H	CH_3	—	1.98	1.68	[33]
5	CH_3	CH_3	1.47	2.20	1.85	[27]
5	CH_3	CH_3	1.54	2.07	1.76	[33]
6	H	H	2.02	3.05	1.67	[32, 33]
6	CH_3	CH_3	1.60	2.55	2.17	[27]
6	CH_3	CH_3	1.56	2.55	2.10	[33]
7	H	CH_3	1.82	—	—	[32]
7	CH_3	CH_3	1.67	2.87	2.41	[27]
24	H	H	2.88	—	—	[32]
24	CH_3	CH_3	2.55	—	—	[32]
183	H	H	3.70	—	—	[32]
319	H	H	4.08	—	—	[32]
4	$CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$	$CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$	1.25	1.89	1.60	[27]
4	$CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$	$CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$	1.34	1.78	1.56	[27]
			1.44	2.15	1.66	[27]
			1.61	2.83	2.29	[27]
	15-Crown-5		3.25	—	—	[32]
	18-Crown-6		4.35	6.10	4.62	[32, 41]

Crystalline complexes of glymes with alkali and alkaline earth metal cations could not be obtained for a long time.[6,57] However, numerous crystalline complexes of not only glymes but also glycols

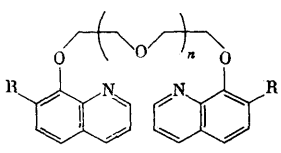
with alkali and alkaline earth metal salts are now known.[25,8–61] These complexes form stoichiometric complexes. They have been synthesised mainly from metal thiocyanates. The interaction of oligo(ethylene glycol) with cations is of the donor–acceptor type and resembles the formation of complexes by macrocyclic polyethers.[6] The structures of certain complexes of oligo(ethylene glycol) have been established by X-ray diffraction.[62–64]

Thus oligo(poly)(ethylene glycol) and their alkyl ethers exhibit complex-forming properties in relation to alkali, alkaline earth, transition, and other metal cations. However, in terms of their complex-forming capacities, these compounds are largely appreciably inferior to macrocyclic polyethers. Only poly(ethylene glycol) and their alkyl ethers with a high molecular weight approach crown-ethers as regards effectiveness.

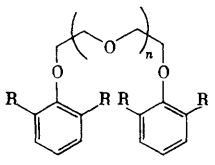
3. Monopodands with rigid end groups

As shown above, only poly(ethylene glycols) with a high molecular weight can to some extent compete with crown ethers (Table 1). According to the concept of end groups proposed by Vögtle,[65] the introduction of aromatic substituents carrying electron-donating centres at the ends of the oligo(ethylene glycol) chain greatly facilitates complex formation. The electron-donating centres of rigid end groups fix the metal cation in the complex formation reaction. The entire ligand molecule can then assume the conformation ensuring the coordination of the electron-donating centres incorporated in the oligo(ethylene glycol) chain. Vögtle and co-workers synthesised in the 1970s a wide variety of aromatic analogues of oligo(ethylene glycol)ethers with rigid groups at one or both ends of the polyether chain.[1] These studies in fact initiated a new stage in the development of podands. There was a transition from solvating solvents to solid complex-forming agents used as solvating additives.

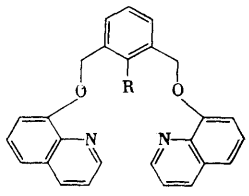
The first representatives of compounds of this type were bis(quinolinyl)oligo-ethers having 8-hydroxyquinoline residues at the ends of the oligo(ethylene glycol) chain structure (I).



(I), $n = 1 \div 6$
$R = H, CH_3$



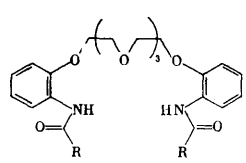
(II), $n = 1 \div 3$
(III), $n = 0 \div 2$



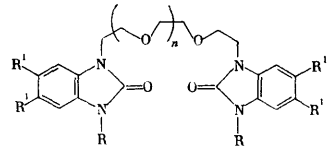
(IV), $R = H, OCH_3, NO_2$

The phenyl, *o*-hydroxy-, *o*-methoxy-, *o*-nitro-, and *o*-ethoxy-carbonyl-phenyl groups [compounds (II)] and the 2,6-dimethoxy-phenyl group [compound (III)] can be used as rigid end groups.[1,42] The flexible glycol units in ligand molecules can be replaced by rigid aromatic units [as in compound (IV)].[57]

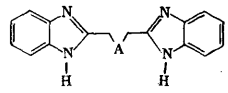
Monopodands with amidophenyl [compound (V)], benzimidazole [compounds (VI) and (VII)], and substituted thiadiazole end groups are known.[65–69] In order to create ligands capable of "becoming adjusted" to various ions, oligo(ethylene glycols) (V), in which R represents a polyether residue with the *o*-nitrophenyl group at the end, were synthesised.[70]



(V)



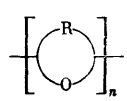
(VI)



(VII)

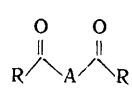
(VI), $n = 0, 1$; $R = R^1 = H, CH_3$;
$R = CH_2CO_2C_2H_5$, $C(CH_3)=CH_2$; (VII),
$A = O, OCH_2CH_2O, S, CH_2SCH_2, 1,2\text{-}OC_6H_4O$.

Podands of a special type were constructed exclusively from cyclooxaalkane segments.[71] Some of these ligands bind metal cations in the same way as crown-ethers, but, in contrast to the latter, they form complexes with a large set of cations.



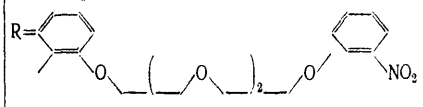
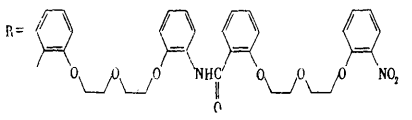
The cation-binding properties of these ligands are manifested particularly clearly when the average length of the segment is sufficient ($n = 6$) and the cyclic units have the *threo*-configuration. Nevertheless, in an experiment on the transport of lithium and potassium picrates from an aqueous solution to chloroform, 18-crown-6 was more effective (63.74%) than the ligand and six tetrahydrofuran units (37.53%) (the amount of the transferred lithium and potassium salt respectively is indicated in brackets).

Ligands with ester groups [compound (VIII)] have been attained by treating alcohols, phenols, and oligo(ethylene glycols) with benzyl chloride, phenylacetyl chloride, or *o*-phenylenedioxydiacetyl chloride.[1,16,72–74]



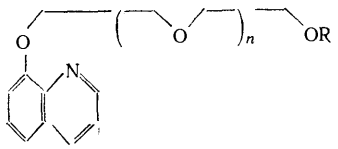
(VIII), $A = (OCH_2CH_2)_nO$, $(n = 1 \div 5)$; CH_2OCH_2; $o\text{-}CH_2OC_6H_4OCH_2$;
$R = OC_4H_9$, $(OCH_2CH_2)_2OC_4H_9$, $2\text{-}R^1C_6H_4$ ($R^1 = H, OCH_3, NO_2$),
$3.5\text{-}(NO_2)_2C_6H_3$, $2.5\text{-}(CH_3)_2C_6H_3CH_2$

Table 2. The logarithms of the stability constants of complexes of monopodands with alkali and alkaline earth metal salts.

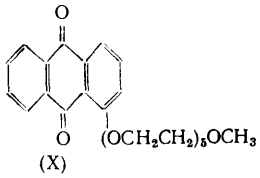
No. of compound	Structure	lg K_{st}								Solvent	Method	Refs.
		Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}			
(I)	$n = 3$, R = H	2.37	3.22	3.51	3.06	2.6	4.99	—	3.87	CH_3OH	A	[33, 75]
(IIa)	$n = 3$, R = R^1 = H	<0	0.7	1.58	0.5	<0	—	—	—	»	»	[75]
(IIb)	$n = 3$, R = H, $R^1 = NO_2$	<1	1.43	1.59	1.93	1.75	—	—	—	»	»	[75]
(V)	$R = CH_3$	—	1.85	—	—	—	—	—	—	C_5H_5N	B	[85]
(V)	»	—	1.53	—	—	—	—	—	—	CH_3CN	»	[70]
(V)		—	2.25	—	—	—	—	—	—	C_5H_5N	»	[85]
(V)	»	—	1.07	—	—	—	—	—	—	CH_3CN	»	[70]
(V)		—	1.90	—	—	—	—	—	—	C_5H_5N	»	[85]
(IX)	$n = 3$, R = Ph	<0.7	1.51	1.87	1.79	1.58	—	—	—	CH_3OH	A	[75]
(XIV)	$n = 0$, X = O, R = R^2 = CH_3, $R^1 = (CH_2)_{11}OC(O)C_2H_5$	1.9	2.1	1.8	1.9	—	3.0	3.3	4.4	C_2H_5OH	C	[86]
(XIV)	$n = 0$, X = O, R = H, R^1 = R^2 = Ph	<1.2	2.4	2.2	2.1	—	2.4	2.9	4.0	»	»	[86]
(XIX)	A = o-C_6H_4, R = R^1 = C_3H_7	1.8	1.0	—	—	—	—	—	—	CH_3OH	A	[75]
(XXVIII)	$m = 2$, R = R^2 = CH_3, $R^1 = C_7H_{15}$	5—6	—	—	—	—	—	—	—	CH_3NO_2	B	[87]
(XXVIII)	»	3	—	—	—	—	—	—	—	CH_3CN	»	[87]
(XXVIII)	»	1.1	—	—	—	—	—	—	—	C_5H_5N	»	[87]
—	Nigericin	—	4.0	5.7	—	—	—	—	—	CH_3OH	C	[41]
—	18-Crown-6	—	4.3	6.1	—	4.6	—	—	—	»	»	[41]

Note. A = spectrophotometry, B = NMR spectroscopy, and C = potentiometry.

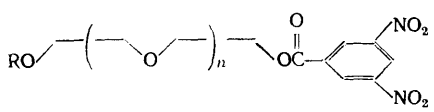
The asymmetric compounds (IX) and (X), containing a combination of different end groups, sometimes a combination of strongly and weakly electron-donating residues, have been synthesised.[42,65,75–79]



(IX), $n = 1-3$, R = H, CH_3, Ph, 2-CH_3O-4-$CH_3C(O)C_6H_3$, 2-$R^1C_6H_4$ ($R^1 = OCH_3$, CN); 1-naphthyl.



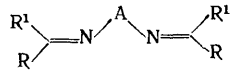
(X)



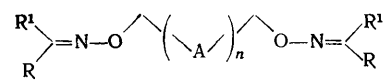
(XI), $n = 2-4$, R = Ph, 2-$CH_3OC_6H_4$, 4-$CH_3OC_6H_4$, 3,5-$(CH_3O)_2C_6H_3$, 1-naphthyl

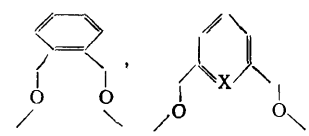
The polyethers (XI), in which electron-donating and electron-accepting groups at the ends of the chains are combined, have been described.[80] The interaction of these compounds with metal cations entails an intramolecular charge transfer. The cationic selectivity of the ligands is inferred from the changes in the electronic spectra.

The open-chain multidentate Schiff bases (XII)—derivatives of diketones, diamines, and aromatic aldehydes—as well as ligands (XIII) in which oxime residues serve as the end groups have been synthesised in order to investigate the influence of the ligand structure on the complex formation reaction.[81,82]



(XII), A = $(CH_2)_n$ ($n = 2$, 3); 2,2'-bisphenylene; R = $CH_2C(O)CH_3$, $CH_2C(O)Ph$, 2-HOC_6H_4, 3-HOC_6H_4, 2-hydroxy-1-naphthylene, 2-pyridyl, 5-(α'-picolinyl), R' = H, CH_3.



(XIII), $n = 1 \div 3$, A = CH_2OCH_2, 

X = N, CH, Cl, $COCH_3$, CNO_2;
R = C (O) CH_3, 2-$R^1C_6H_4$ (R^1 = OH, OCH_3), 4-$CH_3OC_6H_4$, 2-R^1-5-$R^2C_6H_3$ (R^1 = H, OH, CH_3, R^2 = H, OCH_3, NO_2); R^1 = H, CH_3.

The reduction of the ligands (XII) having pyridyl or picolinyl groups at the ends led to the formation of the corresponding tetraamine ligands.[83]

The formation of complexes by certain monopodands in solution has been studied.[70,75,80,84–87] Table 2 lists the logarithms of the stability constants of the complexes of ligands with alkali and alkaline earth metal cations in organic solvents. Metal thiocyanates were used for compounds (I), (II), (IX), and (XIX) as well as nigericin and 18-crown-6. The formation of complexes by the ligands (V) with sodium perchlorate was studied. Lithium, magnesium, and calcium nitrates, sodium, potassium, and rubidium thiocyanates, and barium perchlorate were used for compounds (XIV).

With increase in the strength of the electron-donating properties of the end groups of the ligand (I), (IIa, b), and (IX) with a tetra(ethylene glycol) chain, the stability of the complexes formed by them also increases, as shown by the stability constants. The diphenyl ether of tetra(ethylene glycol) (IIa) exhibits a very weak tendency towards the formation of complexes with alkali metal cations with the exception of potassium. The stability constant of the potassium complex is comparable to those for the ligands (IIb) and (IX). The author suggests that, since the π-electron interaction with the metal ion weakly stabilises the pseudoring, the size of the coordination sphere determines the most favourable conformation of the ethylene glycol chain. On replacement of one phenyl ring by the quinoline group [as in ligand (IX)], the stability constant increases, especially for the large rubidium and caesium cations. The selectivity with respect to potassium is then maintained but is less pronounced than in the case of the ligand (IIa). The introduction of the *o*-nitro-group into the phenyl substituent appreciably improves the complex-forming properties of the podand. The authors explain the preferential formation of complexes by the ligand (IIb) with large cations by the electrostatic repulsion of the *o*-nitrophenyl end groups. The compound with two quinoline end groups [compound (I)] exhibits the most effective complex-forming properties. The partial stacking interaction of the quinoline groups stabilises the pseudocyclic conformation of the complex.[88] Thus the additional electron-donating centres of the rigid end groups play an important role in the stabilisation of the complexes.

Crystalline complexes of monopodands with alkali, alkaline earth, and transition metal ions, lanthanide and actinide ions, and the ammonium cation have been obtained.[1,55,72,77] The complexes are formed as a rule with an exact stoichiometric composition even in the presence of a large excess of one of the components.

Crystalline complexes could not be obtained for analogues of compounds (I)–(III) in which the quinoline and *ortho*-methoxyphenyl end groups are linked by a hydrocarbon chain made up of 8 or 9 carbon atoms.[65,89,90] Crystalline complexes were not obtained for analogues of the ligands (II) with *meta*-methoxy-groups either.[89] Glycols with phenyl end groups [compounds (II)] form crystalline complexes only in the presence of at least five oxygen atoms in the chain.[65,75] Compounds with aromatic bridges, carrying substituents [compound (VII)] also do not afford solid complexes.[57,65]

Open-chain multidentate Schiff bases with various rigid end groups [compounds (XII)] are capable of forming crystalline complexes with transition metal ions.[81,82]

Compounds (XIII) with hydroxyphenyl or methoxyphenyl end groups as well as ligands containing diacetyl monoxime units at the ends of the oligo(ethylene glycol) chain have the (*E*)-configuration and do not form crystalline complexes. Some of them can transfer sodium or potassium permanganate to an organic medium.[82]

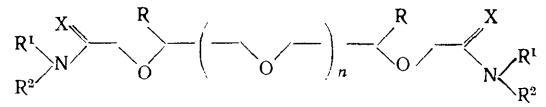
Data on the structures of the complexes of monopodands with alkali and alkaline earth metal ions have been obtained by X-ray diffraction.[1,88,91–94] Podands, which are open-chain ligands, do not have a ready made cavity in which the metal cation could be accommodated. However, during the complex-formation process they form such a cavity in one way or another. The podand molecule can twist into a ring or a helix around the cation.

Podands form crystalline complexes with neutral molecules similar to the crown-ether complexes of the "guest–host" type.[17,95–97]

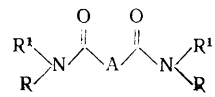
4. Membrane-active monopodands

The ability of podands to interact with metal cations is used in membrane processes. However, there is no direct relation between the effectiveness of the complex-forming agent and its membranotropic properties. Ligands which are effective complex-forming agents for alkali and alkaline earth metal cations are not always good agents for the transfer of ions through membranes. Ion transport can be achieved subject to the condition that the complex formation process is selective and dynamic. It has been shown that[98] there exists a range of optimum stability constants of complexes for the most effective transport of cations. Above and below this range, the rate of transport falls sharply. For a series of alkali and alkaline earth metal cations, ion transport is slight or is altogether absent if the logarithms of the complex formation constants in methanol are less than 3.5–4.0 units.

Open-chain ligands of the amide type with aromatic or hydrocarbon substituents and with a long chain at the nitrogen atom are selective agents transferring alkali and alkaline earth metal ions through liquid membranes [compounds (XIV) and (XV)].[15,16,86,99–105]

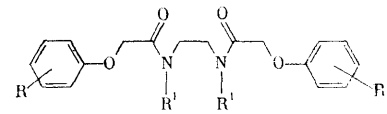


(XIV), $n = 0 \div 2$, X = O, S; $R = R^1 = R^2 = Alk$
$R^1 = (CH_2)_m CO_2Alk$ ($m = 1 \div 11$)



(XV), $A = CH_2OCH_2CH_2OCH_2$, CH_2OCH_2;
$R = CH_3$, $R^1 = C_7H_{15}$, $(CH_2)_5COOC_4H_9$;
$R = R^1 = Alk$, CH_2COOCH_3, Ph

Symmetrical ligands (XVI) containing amide and ether groups are known.[106]



(XVI), R = *o*-NO_2, *o*(*m*)-$NHCOCH_3$, R′ = H, CH_3.

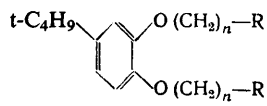
The selectivity of such ionophores with respect to cations is determined mainly by the nature and number of coordination centres and the nature of the substituents at the nitrogen atoms. An increase in the polarity of the ligand molecule leads to the preferential formation of complexes with cations having small radii. The ethylene glycol ligands (XIV) with ω-ethoxycarbonyldecyl, ω-ethoxycarbonylundecyl, or phenyl substituents are selective ligands in relation to alkaline earth metal cations[15,17,86,104] (Tables 2 and 3). The introduction of higher alkyl groups such as hexyl, octyl, decyl, undecyl, and heptadecyl at the nitrogen atom leads to the

Table 3. Potentiometric selectivity coefficients ($K^{pot}_{M_i,M_j}$) of electrodes with liquid membranes containing neutral ligands.

Structure	Material of membrane	M_j									Refs.
		H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	
					(XIV)						
$n=0$, X=O, R=H, $R^1=R^2=C_6H_{13}$	*o*-Nitrophenyl octyl ether	20	$3\cdot10^{-3}$	$5\cdot10^{-2}$	$6\cdot10^{-3}$	$1\cdot10^{-4}$	$8\cdot10^{-4}$	$3\cdot10^{-5}$	1	$3\cdot10^{-1}$	[99]
$n=0$, X=O, R=H, $R^1=(CH_2)_{10}CO_2C_2H_5$ $R^2=CH_3$	*p*-Ethylnitrobenzene	—	$3\cdot10^{-3}$	$7\cdot10^{-3}$	$9\cdot10^{-2}$	$2\cdot10^{-1}$	$6\cdot10^{-2}$	$3\cdot10^{-5}$	1	$8\cdot10^{-2}$	[15]
$n=0$, X=O, $R=R^2=CH_3$ $R^1=(CH_2)_{11}CO_2C_2H_5$	*o*-Nitrophenyl octyl ether	—	$2\cdot10^{-2}$	$1\cdot10^{-2}$	$6\cdot10^{-3}$	$1\cdot10^{-2}$	$9\cdot10^{-3}$	$1\cdot10^{-4}$	1	$1\cdot10^{-3}$	[86]
$n=0$, X=O, R=H $R^1=R^2=CH_2Ph$	Ditto	1	—	1	$2\cdot10^{-1}$	—	—	$3\cdot10^{-4}$	$6\cdot10^{-3}$	$4\cdot10^{-2}$	[17]
$n=0$, X=O, R=H $R^1=R^2=Ph$	»	—	$6\cdot10^{-4}$	$7\cdot10^{-1}$	$3\cdot10^{-1}$	$5\cdot10^{-2}$	$1\cdot10^{-2}$	$4\cdot10^{-5}$	$7\cdot10^{-3}$	1	[86]
$n=1$, X=O, R=H $R^1=R^2=Ph$	»	$9\cdot10^{-2}$	$5\cdot10^{-3}$	$2\cdot10^{-2}$	$4\cdot10^{-2}$	$2\cdot10^{-2}$	$6\cdot10^{-3}$	$4\cdot10^{-5}$	$8\cdot10^{-4}$	1	[104]
$n=0$, X=O, R=H $R^1=C_3H_7$, $R^2=t\text{-}C_4H_9$	»	10	—	$2\cdot10^{-2}$	$2\cdot10^{-2}$	—	—	$3\cdot10^{-4}$	1	$8\cdot10^{-3}$	[17]
					(XVII)						
$n=2$, R=S(O)CH_2Ph	*o*-Nitrophenyl octyl ether	2.6	$3.6\cdot10^{-2}$	$7.4\cdot10^{-3}$	$1.6\cdot10^{-2}$	—	—	$6.8\cdot10^{-3}$	1	—	[102]
$n=3$, R=S(O)Ph	Ditto	$5.4\cdot10^{-2}$	$9.3\cdot10^{-3}$	$1\cdot10^{-3}$	—	—	—	$8.5\cdot10^{-3}$	1	—	[102]
					(XX)						
R=cyclo-C_6H_{11}, R^1=Ph	Bis(1-butylpentyl) adipate	—	4	1	$5\cdot10^{-2}$	$2\cdot10^{-2}$	$8\cdot10^{-3}$	$2\cdot10^{-4}$	$5\cdot10^{-3}$	$5\cdot10^{-3}$	[101]
					(XXVIII)						
$m=1$, $R=CH_3$, $R^1=C_7H_{15}$, $R^2=C_2H_5$	*o*-Nitrophenyl octyl ether	$2\cdot10^{-1}$	2.8	1	$4.4\cdot10^{-3}$	$3.6\cdot10^{-3}$	$2.9\cdot10^{-3}$	$1.7\cdot10^{-3}$	$2.9\cdot10^{-1}$	$4.4\cdot10^{-2}$	[15]
$m=2$, $R=R^2=CH_3$, $R^1=C_7H_{15}$	Dibenzyl ether	—	1	$5\cdot10^{-2}$	$8\cdot10^{-3}$	$5\cdot10^{-3}$	$6\cdot10^{-3}$	$4\cdot10^{-4}$	$8\cdot10^{-4}$	$5\cdot10^{-4}$	[104]
$m=2$, $R=CH_2CH_2OC_2H_5$, $R^1=C_7H_{15}$, $R^2=CH_3$	Soyalipid	—	1	$7\cdot10^{-2}$	$1.6\cdot10^{-2}$	$0.5\cdot10^{-3}$	$8.3\cdot10^{-3}$	—	—	—	[110]
Nonyl phenyl ether of poly(ethylene glycol).$[Ba(BPh_4)_2]_7$	*p*-Ethylnitrobenzene	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$8\cdot10^{-3}$	—	—	$<1\cdot10^{-4}$	$<1\cdot10^{-4}$	1	[15]
Dibenzo-18-crown-6-ether	»	—	—	$4.1\cdot10^{-2}$	1	$3.5\cdot10^{-1}$	$2.7\cdot10^{-1}$	—	—	—	[5]
Valinomycin	Diphenyl ether	$5\cdot10^{-5}$	$2\cdot10^{-4}$	$2.5\cdot10^{-4}$	1	1.9	$4\cdot10^{-1}$	$<2\cdot10^{-4}$	$<2\cdot10^{-4}$	—	[5]

preferential interaction with the calcium cation.[99,106] With increase in lipophilicity, the ionophoric properties of these compounds vanish owing to the kinetically limited exchange reaction between the aqueous phase and the membrane. The dioxadithioamide (XIV) with butyl substituents at the nitrogen atom is a highly selective ionophore for the cadmium ion.[15] The potentiometric selectivity series for this ligand is Cd (1) > Li (1×10^{-3}) > K (8×10^{-4}) > Cs (3×10^{-4}) > Na (1×10^{-4}) = Rb (1×10^{-4}) > Ca (5×10^{-5}) = Ba (5×10^{-5}) > Mg (1.5×10^{-5}). It follows from the data presented that, with the aid of an ion-selective electrode containing a given ligand, it is possible to determine the content of cadmium ions in a mixture with other cations whose concentration is higher by 3–5 orders of magnitude. The *NNN*^{1}*N*^{1}-tetracyclohexyl-substituted diamide (XV) with A = CH_2OCH_2 exhibits selective properties in relation to the calcium ion in the presence of magnesium ions with a separation factor of 10^4.[100]

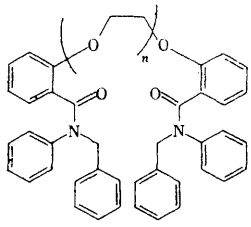
The acyclic polyethers (XVII) with sulphenyl groups are selective in relation to the calcium cation[102] (Table 3).



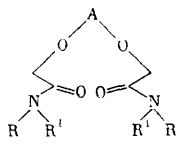
(XVII), R= S(O)C_6H_5, S(O)$CH_2C_6H_5$, S(O)C_8H_{17}-*n*

Ligands with rigid units between the amide end groups [compounds (XVIII)–(XXI)], exhibiting selectivity with respect to sodium in the joint presence of sodium and potassium ions

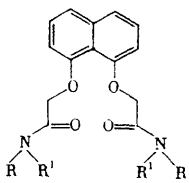
(separation factor of 20), have been obtained.[101,103,107]



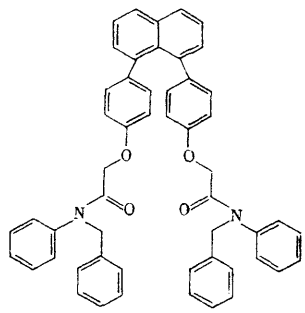
(XVIII)



(XIX)



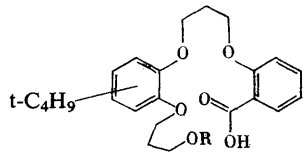
(XX)

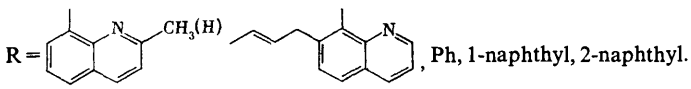


(XXI)

(XVIII), $n = 0$, 1; (XIX), A = 1,2-phenylene, 2,2′-bisphenylene, or 2,3-naphthylene; R = cyclo-C_6H_{11} or Ph, $R^1 = (CH_2)_{11}CO_2C_2H_5$, cyclo-$C_6H_{11}$, or $CH_2C_6H_5$; (XX), $R = R^1$ = cyclo-C_6H_{11}; $R^1 = CH_2C_6H_5$.

Few acyclic ligands selective with respect to lithium ions relative to sodium ions are known.[15,108,109] The creation of lipophilic ionophores for lithium is difficult because the lithium ion has the smallest radius among alkali metals and exhibits a very high capacity for hydration. These ligands are mainly acid in character.

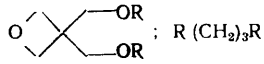




R = , Ph, 1-naphthyl, 2-naphthyl.

Ethylene and tri- and tetra-methylene derivatives have been obtained.[87,110] Ligands with two trimethylene units exhibit the highest selectivity with respect to lithium.

A series of ionophores with a high selectivity with respect to lithium were synthesised recently by the reaction of 3,3-bis(chloromethyl)oxetan or other dihalides with 8-quinolinols.[111]



; R $(CH_2)_3$R

R = 8-quinolinyl.

The selectivity coefficient with respect to lithium relative to sodium is 110 for oxetan with 8-hydroxyquinoline groups. This is the best of the known lithium transferring agents.

The parameters of the membrane electrodes in which neutral complex-forming agents are used are listed in Table 3. The selectivity of the complex formation reaction is influenced by the medium of the membrane. With increase in the polarity of the medium, the stability of the complexes falls.[87]

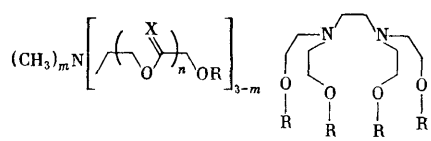
It has been shown by ^{13}C NMR spectroscopy[107,112] that in solution amide ligands of type (XIV) form complexes with ligand : metal = 1 : 1 and 2 : 1 compositions. The amide and ether oxygen atoms and in 1 : 1 complexes the carbonyl groups (as a rule) participate in coordination to the cation. Crystalline complexes with alkaline earth and transition metal salts are stabilised by water molecules.[103]

Monopodands with rigid end groups occupy an intermediate position between oligo(ethylene glycols), on the one hand, and glymes and crown-ethers, on the other, as regards their complex-forming properties. The simplest method of synthesis of monopodands, which does not require a high dilution or the use of a matrix method, and high yields of products are all advantages of the open-chain ligands over their cyclic analogues.

III. Oligo(poly)podands

1. Acyclic analogues of cryptands

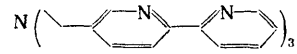
The high complex-forming capacity of bicyclic nitrogen-containing polyethers — cryptands[113] — stimulated the synthesis of their acyclic analogues,[66,114–119] which are open-chain ligands with several polyether chains diverging from the central nitrogen atom. Ligands of this type are combined under the general name oligo(poly)-podands.[2] The oligo(ethylene glycol) chains of these compounds have different end groups. Ligands based on ethanolamines with hydroxy-end groups are known. The alkyl groups in polypodands can be replaced by rigid phenyl, quinolinyl, and tropolone groups [compounds (XXII)–(XXV)].



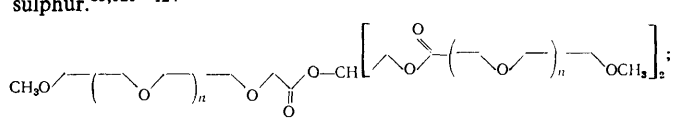
(XXII),(XXIII) (XXIV) (XXV)

(XXII), $m = 1$, $n = 0$, $X = H_2$; (XXIII), $m = 0$, $n = 0-3$, $X = H_2$, O; (XXII)–(XXIV), R = H, Alk, Ph, 2-$R^1C_6H_4$ ($R^1 = CH_3$, OCH_3, NO_2); 2,6-$(CH_3O)_2C_6H_3$, 8-quinolinyl, 2-tropolonyl; (XXV), $n = 0$, 2, R = Alk, CH_2OCH_3, $CH_2(OCH_2CH_2)_2OC_4H_9$, R^1 = Alk.

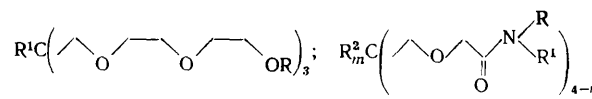
Tri- and tetra-podands containing 4-aminomethylene-2,2′-bipyridyl groups as complex-forming fragments have been synthesised.[120]



The central nitrogen atom in compounds of type (XXII)–(XXV) can be replaced by carbon [compounds (XXVI)–(XXVIII)] or sulphur.[85,121–124]

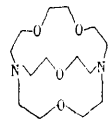
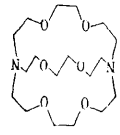


(XXVI), $n = 2$, 3



(XXVII), R = H, Alk, R^1 = Alk (XXVIII), $m = 1$, 2, R = Alk, Ph, R^1 = Alk, R^2 = Alk

Table 4. The logarithms of the stability constants of complexes of polypodands with alkali and alkaline earth metal chlorides.

No. of compound	R	n	lg K_{st}				Solvent	Refs.
			Li^+/Na^+	K^+/Cs^+	Mg^{2+}/Ca^{2+}	Sr^{2+}/Ba^{2+}		
(XXIIa)	8-Quinolinyl	—	<2/<2	<2/<2	<2/<2	<2/<2	$CH_3OH:H_2O$ (88:12)	[115]
(XXIIb)	2-Tropolonyl	—	<2/2.0	<2/<2	<2/2.1	2.5/2.6	»	[115]
(XXIII)	8-Quinolinyl	0	<2/2.7	2.0/<2	2.06/2.14	2.7/3.2	»	[115]
(XXIII)	8-Quinolinyl	0	2.18/3.69	2.58/1.57	—	—	CH_3OH	[75]
(XXIII)	2-Tropolonyl	0	<2/<2	<2/<2	<2/<2	3.3/3.6	$CH_3OH:H_2O$ (88:12)	[115]
(XXIV)	8-Quinolinyl	0	<2/2.1	2.1/<2	<2/<2	2.1/2.8	»	[115]
(XXIV)	2-Tropolonyl	0	—/2.5	—	—/2.7	3.0/3.1	»	[115]
(I) *	8-Quinolinyl	3	2.37/3.22	3.51/2.6	4.99/—	—	CH_3OH	[65, 75]
—		—	7.58/6.08	2.24/<2	4.0/4.34	2.9/<2	$CH_3OH:H_2O$ (95:5)	[125]
—		—	1.8/7.21	9.75/3.54	<2/7.6	11.5/12	»	[125]

* Metal thiocyanates were used as the salts.

The stability constants of the complexes formed by open-chain cryptands with alkali metal, alkaline earth metal, and lanthanide cations have been determined by spectrophotometric[65,75] and potentiometric[115,125,126] methods. The most stable complexes are formed by these ligands with cations having large radii—sodium, potassium, strontium, and barium. The logarithm of the stability constant of the barium complex of the tripodand (XXIII, n = 1) with 8-hydroxyquinoline end groups is 4 units.[127] The end groups play an appreciable role in complex formation. Thus ligands with tropolone groups form more stable complexes than their analogues with quinolinyl groups (Table 4). For ligands with the same number of units in the oligo(ethylene glycol) chain, the stability of the complexes increases with enhancement of the electron-donating capacity of the end group in the sequence C_6H_5 < 2-$NO_2C_6H_4$ ⩽ CH_3 < 2-$CH_3OC_6H_4$ ⩽ 8-quinolinyl.[127] It is of interest that the tetrapodands (XXIV) form more stable complexes than the analogous dipodands (XXII) but less stable than the tripodands (XXIII). This is attributed to the steric hindrance which may be generated by the four bulky end groups.

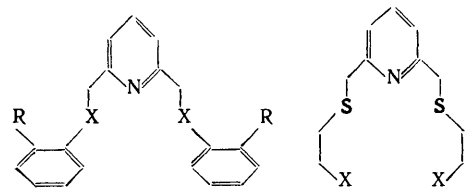
Comparison of the complex-forming properties (Table 4) of the tripodand (XXIII) and the tetraethylene glycol monopodand with quinolinyl end groups [compound (I)], having the same number of electron-donating atoms, shows that in the series of alkali metals this ligand is only slightly superior to the monopodand (I) only in the case of the sodium cation. As regards other di-, tri- and tetrapodands, they all form less stable complexes with alkali metal cations than the monopodand (I). This permits the conclusion that the simpler monopodands are also more effective for alkali metal cations. It is noteworthy that bicyclic nitrogen-containing ligands (cryptands) form very stable complexes with alkali and alkaline earth metal cations[125] but they are difficult to obtain.

In contrast to nitrogen-containing podands, the complex-forming properties of the carbon ligands are much weaker.[85,87] The logarithms of the stability constants of the complexes of the ligands (XXVI, n = 2) and (XXVII) with sodium perchlorate in pyridine are 2.0 and 1.3 respectively.

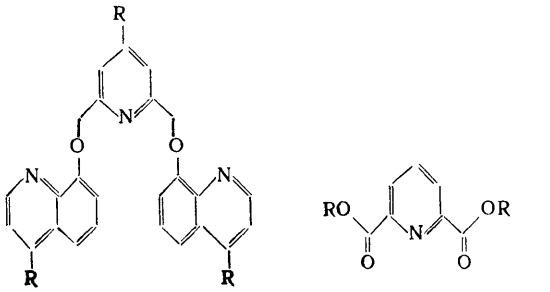
Numerous crystalline complexes with alkali, alkaline earth, transition, and other metal salts have been obtained for the open-chain cryptand analogues.[51,127–129] The tripodand (XXIII, n = 1), having methylquinolinyl groups, forms crystalline complexes with neutral molecules such as those of urea, 4-nitrophenylhydrazine, and water.[17,130]

Compounds whose characteristic structural elements are central pyridine and pyridine oxide units constitute a separate group of acyclic multidentate ligands—dipodands. A general method of synthesis of compounds with one pyridine unit [compounds (XXX)–(XXXII)] consists in the interaction of 2,6-di(halogenomethyl)piperidine with phenols or thiols in the presence of a base.[57,84,114,131] Their oxidation with hydrogen peroxide can afford the corresponding *N*-oxides.[132]

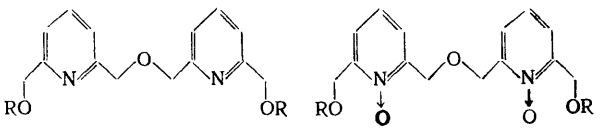
Pyridine ligands with ester groups [compound (XXIII)] have been synthesised.[72] Compounds containing two pyridine or pyridine oxide units [compounds (XXXIV) and (XXXV)] are known.[132–134]



(XXX), X=O, S; R=H, Hal, NO_2, OAlk, CO_2Alk (XXXI), X=H, OH, NH_2



(XXXII), R=H, Cl CH_3O, $N(CH_3)_2$ (XXXIII), R=Alk, $CH_3OCH_2CH_2$, $ClCH_2CH_2$



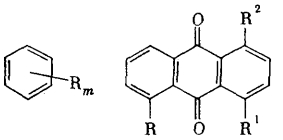
(XXXIV) (XXXV)

(XXXIV), (XXXV), R=H, OH, OAc, 8-quinolinyl, 8-(2-methylquinolinyl), 2-$H_3COC_6H_4$, 2,6-$(CH_3O)_2C_6H_3$.

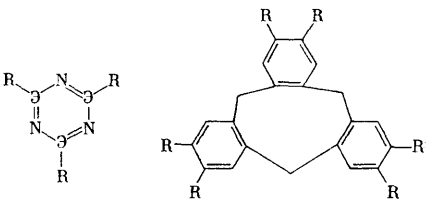
Representatives of compounds of this type form very readily crystalline complexes with alkali, alkaline earth, and heavy metal ions.[15,57,72,84] Ligands with pyridine oxide units exhibit a reduced complex-forming capacity in relation to alkali metal cations.[132] The introduction of pyridine units into the polyether chain imparts rigidity to the ligands, which greatly improves their selectivity in relation to alkali metal cations.[75,84] It is of interest that classical ligands for transition metal ions, such as bipyridyl, terpyridyl, and phenanthroline, form stable complexes with alkali and alkaline earth metal salts.[135,136] Ligands of the ester type (XXXIII) do not form complexes with heavy metals.[72] Certain compounds with pyridine and pyridine oxide units afford crystalline complexes with urea, thiourea, malodinitrile, and water.[132,137]

2. "Octopus-like" polypodands

The number of oligoether chains in polypodands can be increased by combining them with some kind of binding centre. Ligands with six and more multidentate chains whose electron-donating centres consist of oxygen, sulphur, selenium, and nitrogen atoms have been obtained in this way. The benzene ring [compound (XXXVI)] has been used as the binding fragment.[66,138–140] These ligands have been synthesised by treating hexa(bromomethyl)benzene in the presence of a base with the corresponding phenol, thiol, or selenol.



(XXXVI) (XXXVII)

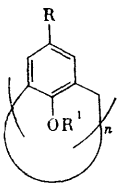


(XXXVIII) (XXXIX)

(XXXVI), $R=CH_2X(CH_2CH_2O)_nAlk(Ph)$, X=O, S, Se, $n=0-3$, $m=2-6$;
(XXXVII), $R=R^1=O(CH_2CH_2O)_3CH_3$, $R^2=H$, $R=R^2=O(CH_2CH_2O)_3CH_3$, $R^1=H$;
(XXXVIII), E=C, P(V), $R=N[(CH_2CH_2O)_4Alk]_2$, $(OCH_2CH_2)_nOAlk$;
(XXXIX), $R=(OCH_2CH_2)_3Alk$.

Treatment of 1,5- or 1,8-dichloroanthraquinone with the monomethyl ether of triethylene glycol in the presence of sodium hydride led to the synthesis of podands[141] with the anthraquinone unit [compounds (XXXVII)].

Polyether chains may be present in triazine, or cyclophosphazene [compound (XXXVIII)] and cycloveratrylene [compound (XXXIX)] systems.[123,142] Oligoethylene glycol units can be combined in a matrix made up of cyclic oligomers obtained under the conditions of base catalysis.[143,144] Multidentate chains are introduced into these compounds instead of hydroxy-groups via the tosylates of the corresponding cellosolves.[145–148] Such macrocyclic compounds have been called spherands or calixarenes (XL).



(XL)

(XL), $n=4, 6, 8$; R = H, Alk; R^1 = Alk, $(CH_2CH_2O)_nAlk$.

Since the complex-forming capacity of these ligands is mainly determined by the structure of the side chains carrying electron-donating centres, they can be regarded as a variety of podands.

The complex-forming capacity of the ligands (XXXVI)–(XXXIX) decreases with decrease in the number of their binding sites. Compounds (XXXVI) with six short chains, terminating in thiophenyl or thiocycloalkyl groups, do not interact with metal ions but do form inclusion compounds with neutral organic molecules.[140,149] "Octopus-like" polypodands whose chains terminate in rigid electron-donating groups form crystalline complexes with derivatives of urea, pyridine, amides, nitriles, diglyme, and crown-ethers.[150] Trisubstituted benzenes do not give rise to inclusion compounds.[139] Crystalline complexes of calcium and barium thiocyanates with a trisubstituted benzene having amide groups have been isolated.[66]

Polypodands based on a cyclic oligomeric matrix — the spherands (XL) — exhibit complex-forming properties in relation to alkali metal cations. The formation of complexes by these compounds with lithium and sodium perchlorates and picrates has been observed by NMR spectroscopy.[151,152] The sodium complex of a calix[4]arene ($R^1 = CH_3$), in which the sodium ion interacts with all four oxygen atoms, has been isolated.[153] The high selectivity of spherands based on anisole with $n = 6$ in relation to lithium and sodium ions in the series of alkali metals has been demonstrated.[154] There exist data indicating a high extracting capacity of spherands with $n = 6$ and 2-methoxy-groups in aromatic rings in relation to guanidine.[147] However, the complex-forming capacity of these compounds is appreciably inferior to that of its analogues in which R^1 consists of ester or amide groups.[148,153,155–157]

Thus the increase in the number of binding sites in the ligands achieved by including additional oligoethylene glycol chains in the podand molecules constitutes yet another way of enhancing their complex-forming properties. The replacement of electron-donating ether oxygen atoms by other heteroatoms or groups with an enhanced nucleophilicity also makes it possible to improve the complex-forming capacity of podands. However, the increase in the complexity of the structure of such ligands makes them less available.

IV. Applications of neutral acyclic complex-forming agents

At the present time, the number of studies devoted to the practical use of podands is small but these compounds have considerable potential possibilities for applications in chemistry and technology. The most thoroughly investigated field in which podands are used is phase transfer catalysis, which constitutes a promising method for effecting chemical reactions.[9–12] Oligo- and poly-ethylene glycols accelerate the nucleophilic substitution reactions at a carbon atom between anions and water-insoluble neutral organic compounds in two-phase systems. Systems incorporating different potassium salts, carboxylic and sulphonic acid chlorides, and alkyl halides have been investigated[29,32,76,158–165] (Table 5). The effectiveness of oligo- and poly-ethylene glycols and their ethers increases with increase in concentration and in the molecular weight of the ligand. Polyethylene glycols with a molecular weight in excess of 400 can be used as phase transfer catalysts (Table 5) whose activity depends on the specific system. The increase in the rates of nucleophilic reactions in the presence of polyethylene glycols has been explained by the cooperative solvation of alkali metal cations by oxygen atoms leading to the activation of the anions.[166]

The use of monopodands based on catechol with quinolinyl end groups as phase transfer catalysts increases by a factor greater than 2–3 the yield of the product (Table 5). The application of "octopus-like" ligands (XXXVI) in reactions of alkyl halides with potassium cyanide increases the yield by a factor of 10.[167] Derivatives of 1,3,5-triazine (XXXVIII) proved to be effective catalysts in any anionic reactions.[123,142] The activity of these ligands increases with increase in the number of binding sites of the oligoethylene glycol chains and also in the length of the alkyl groups at their ends. The catalytic properties of triazine ligands resemble those of tetraalkylphosphonium salts. Comparison of the catalytic activities of crown-ethers, cryptands, glymes, and poly(ethylene glycols) showed that the cryptand 222 is the most effective. Decaglyme is not inferior to 18-crown-6-ether and tetrabutylammonium perchlorate, while the effectiveness of poly(ethylene glycol) (Carbowax-20M) is similar to that of dibenzo-18-crown-6 [163] (Table 6).

Table 5. Yields of products in certain nucleophilic substitution reactions using podands as phase transfer catalysts.

Catalyst	Structure	Reaction conditions	Yield, %
$C_4H_9Br + KI \rightarrow C_4H_9I + KBr$ (Ref.159)			
—	—	1.5 h, refluxing, water	13
$HO(CH_2CH_2O)_3OH$	—	ditto	27
PEG-1000	—	»	50
PEG-2000	—	»	96
PEG-6000	—	»	96
Dibenzo-18-crown-6	—	»	45
$C_6H_5CH_2Br + CH_3COOK \rightarrow C_6H_5CH_2OCOCH_3 + KBr$ (Ref.164)			
$H_3CO(CH_2CH_2O)_8CH_3$	—	CH_3CN, 1 h, 20 °C	96
18-Crown-6	—	CH_3CN, 2 h, 25 °C	100
$C_6H_5CH_2Cl + CH_3COOK \rightarrow C_6H_5CH_2OCOCH_3 + KCl$ [76]			
—	—	CH_3CN, 2 h, refluxing	29
(IX)	n=2, R=$CH_3C(O)$	ditto	98
	n=3, R=$CH_3C(O)$,	»	88
	2-CH_3O-4-$CH_3C(O)C_6H_3$	»	68
$n\text{-}C_8H_{17}Br + KI \rightarrow n\text{-}C_8H_{17}I + KBr$ (Refs. 123, 142)			
(XXVII)	R=CH_2CH_2OH; R^1=$CH_2OC_{10}H_{21}$	H_2O, 72 h, 60 °C	87
»	R=n-$C_8H_{17}OCH_2CH_2$ R^1=$CH_2OC_{10}H_{21}$	H_2O, 10 h, 80 °C	<1
(XXXVIII), E=C	[n-$C_4H_9(OCH_2CH_2)_4]_2N$	H_2O, 72 h, 60 °C	82
»	[n-$C_8H_{17}(OCH_2CH_2)_4]_2N$	H_2O, 3 h, 60 °C	85
(XXXVIII), E=P(V)	n-$C_8H_{17}(OCH_2CH_2)_3O$	»	42
»	n-$C_8H_{17}(OCH_2CH_2)_2O$	H_2O, 8 h, 80 °C	88
$(C_4H_9)_3C_{10}H_{21}PBr$	—	H_2O, 3 h, 60 °C	72

The catalytic activity of glymes with $n = 1-4$, 10, 21 in the aminolysis of esters[168] is higher than that of crown ethers with the same number of oxygen atoms (Table 6).

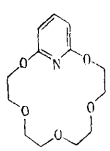
Poly(ethylene glycols) and their ethers can be used as phase transfer catalysts in *N*- and *S*-alkylation reactions.[169–172]

The tripodands (XXIII, $n = 1$, $m = 0$, $X = H_2$) constitute a new class of phase transfer catalyst in a solid–liquid system.[173]

An important field where podands can be used is extraction. Thus poly(ethylene glycols) containing more than 23 units exhibit strong extracting properties in relation to potassium, which are comparable to those of 18-crown-6[174,175] (Table 7). Poly(ethylene glycols) with molecular weights ranging from 400 to 4000 are more effective extractants for lead and strontium than dibenzo-18-crown-6

and dibenzo-24-crown-8 but are inferior to 18-crown-6.[176,177] Oligo(ethylene glycols) with nitrile end groups can be used to extract alkali metals from boracic water in the presence of a large excess of alkaline earth elements.[178] The sulphur-containing podand 1,12-di-2-thienyl-2,5,8,11-tetrathiadodecane extracts silver ions quantitatively from dilute aqueous solutions.[179] An asymmetric monopodand, at the ends of oligo(ethylene glycol) chain (n = 11) of which there are substituted aryl groups, extracts alkali and alkaline earth metal cations with formation of 1 : 1 complexes.[180]

Table 6. Catalytic activities of different catalysts.

Catalyst	Relative rate of reaction
$KSCN + n\text{-}NO_2C_6H_4CH_2Br \xrightarrow{CHCl_3-H_2O} n\text{-}NO_2C_6H_4CH_2SCN +$ + KBr (Ref.163)	
18-Crown-6	1.44
Benzo-18-crown-6	1.23
Dibenzo-18-crown-6	1.00
Dicyclohexyl-18-crown-6	1.65
Cryptand 222	5.10
Decaglyme	1.41
$(C_4H_9)_4NClO_4$	1.29
Carbowax 20 M	0.88
$CH_3COOC_6H_4NO_2\text{-}p + NH_2C_4H_9 \xrightarrow{PhCl} p\text{-}HOC_6H_4NO_2 +$ + $CH_3CONHC_4H_9$ (Ref.168)	
$CH_3(OCH_2CH_2)_nOCH_3$	
n=1	1
n=2	4.9
n=3	11
n=4	14
n=10	37
n=22.3	76
6-Crown-2	0.52
9-Crown-3	2.8
12-Crown-4	5.2
15-Crown-5	8.8
	0.29

Another possible application of podands is association with their ability to solubilise salts in solvents of low polarity. This makes it possible to carry out a whole series of reactions under homogeneous conditions in non-polar media. The nitrogen-containing tripodands (XXIII) transfer potassium permanganate and alkali metal picrates to the organic phase much more readily than dibenzo-18-crown-6.[118] In the presence of poly(ethylene glycols), it is possible to dissolve metallic potassium in benzene[181] and potassium permanganate in organic solvents[182] and alkenes can be oxidised by potassium permanganate.[160,161]

A series of applications of podands are associated with their membrane activity. Some of them can be used in cation-sensitive membrane electrodes specific to alkali and alkaline earth metal ions (Table 3). Thus the complex $Ba(BPh_4)_2$ with nonyl phenyl ether of poly(ethylene glycol) (n = 30) is used in a barium-sensitive electrode.[15] The neutral acyclic diamide [XIV, n = 0, X = O, R = CH_3, R^1 = $(CH_2)_{10}COOC_2H_5$] is used in a calcium-selective electrode.[5] Many polydentate ligands, such as the oxa-analogues of diamides of sebacic and azelaic acids (XIV), are known. They are selective transferring agents for lithium and sodium ions in the presence of protons and calcium, strontium, and barium ions.[15,17,86,99–101,104,108,183] A study of the membrane activity of tetraethylene glycol with quinoline end groups showed that this ligand transfers ammonium cations selectively through a liquid membrane in the presence of alkali metal ions.[184] The tripodand (XXIII, n = 1, X = H_2) exhibited effective and specific transport properties for silver ions.[119] Podands of the type of spherands (XL) can also be used in membranes.[144]

Table 7. The extracting capacities of certain ligands in relation to alkali metal salts in the H_2O-CH_2Cl system.[174,175]

Ligand	c_L, M	% in CH_2Cl_2		
		0.85×10^{-4} M Na picrate	0.95×10^{-4} M K picrate	1.0 M KSCN
	—	0.7	0.7	—
15-Crown-5	0.00058	1.5	1.7	—
18-Crown-6	0.00056	2.4	17.3	—
PEG-400	0.02	—	—	6
PEG-600	0.02	—	—	14
PEG-1000, n=23	0.00047	2.0	8.2	—
Ditto	0.00181	3.9	14.5	—
"	0.02	—	—	27
PEG-4000	0.02	—	—	100
PEG-6800	0.00027	3.6	19.2	—
"	0.00036	4.7	20.8	—

The great variety of structures of the neutral acyclic polydentate ligands makes it possible to vary their selectivity with respect to cations within wide limits. The ability of podands to form complexes with neutral organic molecules can be of pharmacological interest, particularly in the case of urea. Furthermore, the availability of these compounds makes them promising complex-forming agents which can find applications in various branches of chemistry and the national economy.

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During the preparation of the manuscript for the press, new studies on the synthesis of podands, on their complex-forming properties, and on their applications in organic synthesis were published. Thus these questions are discussed in a book.[185] New Schiff bases capable of combining in complexes transition and alkali or alkaline earth metal ions simultaneously have been synthesised.[186–188] Podands with imidazole units have been obtained and their transport properties in relation to alkali metals and ammonium cations have been investigated.[189–191] The synthesis

of chiral podands derived from carbohydrates[192–194] and from the 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene fragment[195] are being developed. A chiral ligand coordinating the lithium cation has been put forward.[196] New tripodands of type (XXVII) are selective complex-forming agents in relation to cations with a small radius.[197] Monopodands with different end groups have been obtained by opening epoxide rings in the diglycidyl ethers of poly(ethylene glycols).[198] The synthesis of new sulphonamide podands,[199] compounds based on 1,4-benzoquinone,[200] cyclohexane,[201] and a phosphazene matrix,[202] and open-chain analogues of benzo-crown-ethers[203] have been described. A report has been published on the synthesis of a new class of branched polyethers—the so-called dendrimers and arboreols.[204] Dendrimers have a spherical steric oligomeric structure. Some of them (arboreols) contain a large number of terminal OH groups.

The study of the formation of complexes by oligo- and poly-(ethylene glycols) and their ethers with alkali metal and ammonium ions[205,206] and of tripodands having a central carbon atom with the Fe^{3+} and Ga^{3+} cations by various physicochemical methods is being continued.[207] The structures of complexes of tetraglyme with the oxonium cation,[208] of penta- and hexa-glymes with calcium, strontium, and barium thiocyanates,[209,210] and of triethylene glycol with lanthanide chlorides[211] have been established. The complex-forming properties of their sulphur-containing analogues are being investigated.[212,213] The interaction of amino-derivatives of oligo-(ethylene glycol) with alkaline earth and transition metal ions is being studied vigorously.[214–219] New data have been obtained on the behaviour in solution of polyamines with various end groups in the presence of transition and other metal cations.[220–223] Their complexes with the lanthanides[224] and rhenium(V)[225] have been synthesised and characterised.

The properties of podands of different types as phase transfer catalysts are being investigated. In the presence of poly(ethylene glycols) and their derivatives, nucleophilic substitution reactions,[226–228] oxidation reactions of cyclic ketones,[229] and the dissolution of metals[230] are accelerated and oxidation-reduction processes are promoted.[231] There are new examples of the use of ligands of type (XXXVIII)[232] and of calixarenes (XL) with oligoethylene chains in the formation reactions of ethers.[233]

The extracting properties of hydrophobic dialkyl ethers of oligo-(ethylene glycols)[234] and of their analogues with electron-donating S and N atoms[235–237] in relation to alkali and alkaline earth metal cations are being investigated in relation to the similar properties of macrocyclic ligands.

Podands which could be used as electrode-active components of membranes of ion-selective electrodes are being sought.[238–239]

A method of synthesis of solid complexes of organomagnesium compounds with tris(dioxa-3,6-heptyl)amine has been described.[240] The first photophysical study of complexes of podands, coronands, and cryptands in photoelectron transfer reactions has been noted.[241]

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The use of microorganism cells immobilised in carrageenan for the synthesis of organic substances

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ABSTRACT. The present state of the problem of the use of immobilised cells of microorganisms for the synthesis of organic substances is analysed. The physicochemical properties of carrageenan and the characteristic features of the immobilisation of microorganism cells in carrageenan are examined and a systematic account is given of the results of treating carrageenan and the immobilised preparations with stabilising reagents.

The bibliography includes 112 references.

CONTENTS

I. Introduction 299
II. Physicochemical properties of carrageenan and the characteristic features of the immobilisation of microorganism cells in carrageenan 300
III. The use of microorganism cells immobilised in carrageenan for the synthesis of organic substances 302

I. Introduction

It is generally known that all biochemical reactions in nature and approximately 80% of industrial processes are effected by virtue of catalysis. Biocatalysts (especially the cells of microorganisms), which possess a high catalytic activity, specificity, and the ability to effect processes at the usual temperatures, have become the objects of close attention in recent years. The advances in the chemistry of steroids, where biocatalysts are widely used, clearly demonstrated their advantages over chemical reactions. However, the use of biocatalysts for the specific transformation of organic substances has been significantly restricted by the specific features of experiments involving them, by the fact that particular classes of compounds were studied, by their lability, by the difficulty of separating them from the reaction products, and in many cases by their low economic effectiveness because they are used only once.

The employment of biocatalysts developed extensively following the discovery of the possibility of immobilising them, as a result of which during the last 10–15 years they have been deliberately prepared in the form immobilised on a carrier or in a gel.[1–15] Special attention has been devoted to the creation of highly effective biocatalysts based on immobilised cells of microorganisms.

About 100 laboratory procedures for the use of immobilised microorganism cells in fine organic synthesis for the preparation of organic acids, solvents, methane, hydrogen, ethanol, enzymes, antibiotics, aminoacids, pantothenic acid, glutathione, and steroids and also for the purification of waste water are now known. Several of these processes have found practical application on an industrial scale: in the preparation of aspartic and malic acids, of lysine from caprolactam, and of leucine and ethanol.[16] A factory manufacturing phenylalanine with an annual output of 600 tonnes has been working in the USA since 1984, while in Japan not only aminoacids but also ethanol and acrylonitrile are produced with the aid of immobilised microorganism cells.

This can be explained by a whole series of advantages of the use of immobilised cells compared with the use of immobilised enzymes and ordinary cells.[17–19]

1. The lack of expenditure on the isolation and purification of enzymes.
2. The higher stability and activity compared with immobilised enzymes and free cells, since immobilisation protects the cells against external influences.
3. The reduction of expenditure on the isolation and purification of reaction products, since they are isolated from the biomass and the metabolic products of the microorganism.
4. The possibility of creating continuous automated manufacturing processes in which inhibition by both the substrate and by the reaction products is diminished.
5. The ability of polyenzyme systems to function for a long time and the regeneration of cofactors.
6. The possibility of reducing the volumes of the reactions effected by immobilised cells compared with free cells.
7. The improvement of the possibility of monitoring the reaction.
8. The likely significant diminution of the contamination of the environment.
9. A significant decrease in the cost of the reaction products.

However, despite the increasing number of publications on the immobilisation of microorganism cells, the results of this process and of the use of immobilised microorganism cells are unpredictable and are determined primarily by the ability of the cell to retain on immobilisation and in the immobilised state a specific activity and to operate stably in a specific process. They depend on a very large variety of factors. Virtually all the existing immobilisation methods have definite advantages and disadvantages. The commonest method involves incorporation in a gel. It ensures repeated use without the separation of the cells and repeated sowing of the medium, a high concentration of cells in the carrier, and the employment of highly productive reactors, but it is also distinguished by an increased resistance to mass transfer, because the substrates and products have to diffuse into the gel and out of the gel. The

physicochemical parameters of the microenvironment (for example, the pH) in the carrier particles can differ significantly from the corresponding characteristics of the medium outside the particles. Microorganisms can elute from the particles in the course of the experiments. This method is also restricted by the need to use substrates with a low molecular weight. The growth of the microorganism cells and the formation of CO_2 frequently disrupt the gel.

For incorporation in a gel, the most suitable physicochemical properties are those of polyacrylamide gel,[4,20,21] polyurethane,[3] collagen,[6] agar,[7,8] gelatine,[9,10] cellulose,[22] alginates,[12,23] and carrageenan.[13–15]

The characteristic features of polyacrylamide gel are the difficulty of obtaining regular spherical particles and the low activity of the resulting preparations, usually owing to the toxic effect on the cell by the gel components: acrylamide, *NN'*-methylenebisacrylamide, and $K_2S_2O_8$. However, the effective mechanical properties and the possibility of regulating the gel network together with data on the multiplication of the cells in the gel have aroused an increased interest by investigators in the use of this gel.[1,16,24–26]

The advantage of agar consists in the rapid growth of new cells in the gel, but its disadvantage is its brittleness. The strength of the gel rapidly falls as cells grow and CO_2 is formed.[27]

The problem with calcium alginate is its instability in the presence of phosphate buffers and certain cations: Mg^{2+}, K^+.[28,29] The gel breaks down fully in 0.1 M K_2HPO_4/KH_2PO_4 solution after 15 min,[29] while phosphate is one of the principal nutrients of microbial cells.

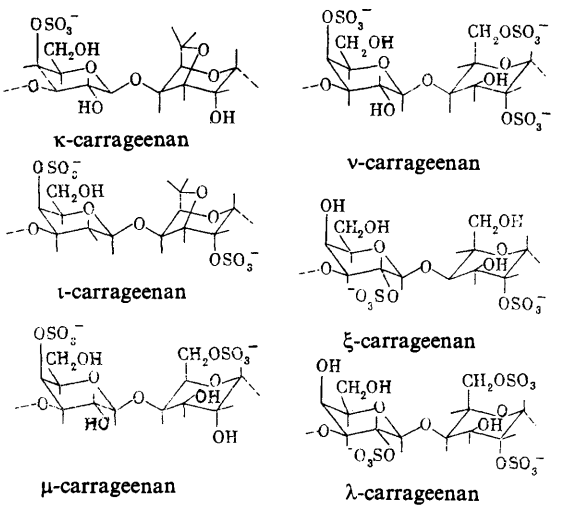
So far there is no universal carrier for the immobilisation of microorganism cells nor is there a universal immobilisation method. However, analysis of data on immobilisation in carrageenan showed that its practical use is promising, since the Japanese research laboratory of the Tanabe Seiyaku Company reported the successful incorporation of more than 50 microorganisms in this gel.

In the present review, an attempt is made to survey and describe systematically the results of experimental studies which make it possible to justify the employment of carrageenan as an immobilisation matrix, as well as data on the use of microorganisms immobilised in carrageenan for the synthesis of organic substances.

II. Physicochemical properties of carrageenan and the characteristic features of the immobilisation of microorganism cells in carrageenan

Carrageenans are sulphate derivatives of polysaccharides obtained from the red seaweed *Phodophyceae* and *Ginartinaceae*.[30] The annual manufacture of carrageenans is on a scale not smaller than that of agar. The principal consumer of these polysaccharides is the food industry, where they are used as gel-forming agents for the preparation of confectionery, milk products, dough, and meat preserves.[17,30,31]

In contrast to agar, carrageenans include, apart from D-galactose, also 3,6-anhydro-α-D-galactose and a much larger amount (20–30%) of sulphate groups[32–34] (MW = 100 000–800 000). The limiting structures of carrageenans can be represented by the following formulae:



The real polysaccharides of the carrageenan group can be very close to one of the formulae represented in the scheme above, but they are usually molecular hybrids—combinations of two and more limiting structures. Only biopolymers characterised by the limiting "kappa" and "iota" structures are able to form gels. Their characteristic feature is the formation of thermoreversible gels under certain conditions. This distinguishes the polysaccharides of the carrageenan group from neutral gel-forming polysaccharides of the agarose group.

According to modern ideas, on extraction of carrageenans from seaweed, their ordered structure breaks down with formation in aqueous solutions of a disordered conformation, which is subsequently restored on formation of a gel and drying until solid. Intermolecular packed structures close to or identical to those *in vivo* are then formed.[35]

The specific nature of the ordered structure depends on the geometry of the covalent bonds between each residue of the primary structure.[36] Carrageenans are made up of six-membered (pyranose) rings having a geometry of the chair type[37] and connected by equatorial bonds. However, the bonds between the carbohydrate rings are not parallel, which leads to the formation of a "bend" and the ordered conformation is in this case helical.[35] X-Ray diffraction data and the temperature dependence of the optical rotation confirm the formation of a double helix for κ- and ι-carrageenans. Despite the existence of hypotheses which tend to explain the nature of intermolecular interactions inducing gel formation, at the present time this question has not been finally resolved. Studies designed to elucidate the causes of the increased stability of carrageenan gels have demonstrated the necessity for the optimum ratio of the length of blocks of the regular structure which are capable of association (and their optimum distribution along the polymer chain) to the length of sections with a masked regularity.[38] The gel formation inducing agents are metal ions—Ca^{2+}, K^+, and Rb^+ for ι-carrageenan and K^+ for κ-carrageenan (other ions exhibit a weaker effect). An X-ray diffraction study of the Ca^{2+} salt of ι-carrageenan showed that in this case the double helix is more extended than in agarose, as a result of which it has no central cavity in which bound water could be inserted. The factor stabilising the ordered structure is the hydrogen bond between the O(2) and O(6) residues of D-galactose in different chains. Since the only unsubstituted hydroxy-groups are present here, the double helix

of ι-carrageenan is structurally completely bound by hydrogen bonds, in contrast to κ-carrageenan. Bearing in mind the large distance between the chains, it is unlikely that the van der Waals forces play an important role in the formation of the helix. However, the ionic interaction is undoubtedly important, each Ca^{2+} ion being linked to two sulphate groups in different helices.[39]

On substitution of Ca^{2+} by univalent cations, a similar structure can be formed in κ-carrageenan, in which there is no second sulphate group. Direct spectroscopic proof of the interaction of K^+ with the sulphate groups of κ-carrageenan has been obtained from the IR spectra of the solutions.[35] Whereas under severe conditions the formation of the double helix in κ- and ι-carrageenans can be induced by ions which are bound non-specifically, under normal conditions cations of suitable size are necessary. The reason for such cationic specificity is evidently the conformational and configurational features of ι- and κ-carrageenans, although it has still not been fully explained.

The polysaccharides from the Black Sea phyllophora can also be classified as carrageenans, since their carbohydrate skeleton is made up of only β-D-galactose and 3,6-anhydro-α-D-galactose joined by alternating α(1) → (3) and β(1) → (4) bonds. The contents of suphate groups in the polysaccharides vary significantly as a function of the phyllophora species (from 17.8 to 27.2%). The different contents of 3,6-anhydro-α-D-glactose and different distributions of the sulphate groups along the carbohydrate skeleton are also characteristic of polysaccharides from different phyllophora species.[38,40] Carrageenans from different phyllophora species show significant differences in their structure and therefore also differ in their physicochemical properties.[41,42]

Table 1. Immobilisation of enzymes and microorganism cells in carrageenans.[48]

Enzymes and microogranisms	Enzyme activity[a]		Yield, %
	before immobilisation	after immobilisation	
Aminoacylase	20	10	50.0
Aspartase	650	300	46.2
Fumarase	360	260	61.5
E. coli (aspartase)	65000[b]	30400	46.8
B. ammoniagenes (fumarase)	9670[c]	5800[d]	60.0
S. phaeochromogenes (glucose isomerase)	7910	4280	54.1

[a] Enzyme: μmol h^{-1} (mg of protein)$^{-1}$; microbial cells: μmol h^{-1} (g of cells)$^{-1}$.
[b] After ultrasonic treatment.
[c] In the presence of bile extract.
[d] After treatment with bile extract.

Microorganism cells are immobilised in κ- and ι-carrageenans, κ-carrageenan being used most often.[13,14,17,18] In studies on the immobilisation of cells in the USSR, carrageenans are little used and Soviet carrageenans are hardly used at all.[43–47] This is incomprehensible, since this method is carried out under mild conditions, simple, and is susceptible to the development of an appropriate technology. The immobilisation of cells in carrageenans consists of virtually two stages: the preparation of a suspension of cells in the carrageenan solution and gel formation. If the stability of the gel is inadequate, the gel has to be stabilised.

It is noteworthy that microbial cells are mixed with the carrageenan solution at 40 °C, the cells of different microorganisms being stable in carrageenan at this temperature; the mixture formed is readily converted into a gel. The gel does not break down during the enzymic reaction, withstands variations in pH, and the size of the pores within the given gel is sufficiently small for enzymes and cells not to leave the gel matrix, while low-molecular-weight substrates and products readily pass through it. Both enzymes and whole cells with a high degree of retention of the initial activity (40–60%) can be immobilised by this method (Table 1).[27,48]

The possibility of immobilising various microorganisms in carrageenan has been demonstrated:[27] *Achromobacter aquatilis, A. liquidum, Aspergillus oryzae, A. niger, Bacillus megatherium, B. subtilis, B. succinium, Brevibacterium ammoniagenes, B. flavum, Corynebacterium glutamicum, Erwinia herbicola, Escherichia coli, Gluconobacter melanogenus, Lactobacillus bulgaris, Micrococcus ureae, Penicillium vinaceum, Proteus vulgaris, Pseudomonas aeruginosa, P. dacunhae, P. putidum, Sarcina lutea, Streptomyces griseus, S. phaeochoromogenes, Serratia marcescens.*

Table 2. Influence of the conditions in the formation of the κ-carrageenan gel on the strength of the latter.[48]

Gel formation conditions	Strength of gel
Cooling to 10 °C	+
Treatment with NH_4Cl	+++
Treatment with metal salts: LiCl, NaCl;	–
KCl, RbCl, CsCl;	++++
$MgCl_2$, $SrCl_2$, $MnCl_2$, $FeCl_2$, $BaCl_2$	
$CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $Pb(CH_3COO)_2$	++
Treatment with amines:	
Methylenediamine, ethylenediamine, p-phenylenediamine, δ-hydroxy-L-lysine, L-lysine hydroxamate, L-histidine hydroxamate *S*-2-aminoethyl-L-cysteine;	+++
hexamethylenediamine, octamethylenediamine, 4-guanidinobutylamine, histidine, DL-histidine hydrazide;	++++
L-ornithine, L-lysine, L-tryptophan hydroxamate	++
Treatment with organic solvents miscible with water: methanol, ethanol, acetone	++

Note. Gel strength: (+), load from 100 to 200 g cm^{-2}; (++), 200 to 500 g cm^{-2}; (+++), 500–1000 g cm^{-2}; (++++), 1000 to 1500 g cm^{-2}; (–), no gel formation.

In order to obtain more stable gels with incorporated *S. phaeochromogenes* cells, a study was made of the influence of the conditions for the formation of the carrageenan gel (Table 2) and in addition also of the influence of the anions of the potassium salts: CO_3^{2-}, SO_4^{2-}, $S_2O_8^{2-}$, PO_4^{3-}, $P_2O_7^{4-}$, $Al_2(SO_4)_4^{2-}$, $Fe(CN)_6^{3-}$, CH_3COO^-, and $^-OOC-COO^-$. Significant differences between the stabilities of

the gels were not found when different anions were used, whereas it follows from the data in Table 2 that more stable gels are formed on contact with KCl, RbCl, CsCl, hexamethylenediamine, octamethylenediamine, agmatine, histamine, and DL-histidine hydrazide. Unfortunately these data do not make it possible to understand the reason for such stabilisation of the gel, nor do they reflect the influence of the gel formation conditions on the retention of the initial activity of the microorganism cells. However, there is no doubt that the stability of the carrageenan gel can be regulated, which encouraged investigators in the search for a more technological solution for specific processes with participation of microorganism cells immobilised in carrageenan.

Thus treatment with stabilising reagents (hexamethylenediamine and glutaraldehyde) made it possible to increase the operational stability (half life) of *E. coli* cells (aspartase activity) in carrageenan from 50 days for untreated cells to 686 days,[48] in the case of *S. phaeochromogenes* (glucose isomerase activity) the increase was from 150 to 260 days, while treatment with gelatine and glutaraldehyde resulted in an increase to 532 days.[49]

Treatment of κ-carrageenan with amines, proposed by Takata et al.,[50] increased the operational stability of immobilised *Brevibacterium flavum* cells without reducing the initial activity.

Interesting results were obtained following the addition of polycationic polymers: the fumarase activity of *B. flavum* cells immobilised in κ-carrageenan in the presence of 0.15% of polyethyleneimine was distinguished by an increased stability to changes in external factors and temperature.[51]

Bearing in mind that the melting points of κ-carrageenan gels with immobilised *B. flavum* cells are higher by 20% in the presence of polyethyleneimine than without it, it has been suggested that there is an interaction between κ-carrageenan, polyethyleneimine and *B. flavum*.

An increase in the porosity of the carrageenan matrix was noted after the introduction into carrageenan of tripotassium phosphate,[52] which improved the diffusion of nutrient substances into the gel and the mechanical properties of the latter.

Treatment of carrageenan with epichlorohydrin and with alkylenepolyamide when *Aspergillus niger* and *Saccharomyces cerevisiae* are incorporated also leads to positive results.[53]

A new method for the stabilisation of microorganism cells immobilised in carrageenan, consisting in the treatment of the gels with polyacrylamide, is noteworthy. For this purpose, acrylamide, *NN'*-methylenebisacrylamide, and β-dimethylaminopropionitrile are allowed to diffuse into the carrageenan grains with subsequent polarisation.[54]

It has also been suggested that the cells be subjected to an activating treatment with NaCl solutions before being incorporated in carrageenan.[55]

Reliable physicochemical evidence which would account for the results of studies on the stabilisation of the carrageenan gel and for the increased operational stability of the immobilised cells as a result of the chemical modification of the gel has not so far been obtained. As a result of the large number of criteria which must be taken into account and the unpredictable behaviour of a specific enzyme activity on immobilisation, it is at present difficult to give preference to any stabilising procedure. The attempts to resort to the ζ-potential of the cells in order to select the immobilisation conditions have also not been convincing.[56] However, it is clear that the gel of the carrageenan matrix plays an important role in the stabilisation of the incorporated microorganism cells, while dissolved carrageenan has no stabilising effect.[31]

Numerous studies have demonstrated that cells can grow in a carrageenan gel at the same rate as the free cells, while in many instances their growth is better: in the stationary growth phase, the number of live yeast cells in the gel was ten times greater compared with the native cells.[57] Similar results have been obtained for *S. carlsbergensis*[58] and *E. coli*.[14] The growth is concentrated in the surface layer of the gel, as a result of which the diffusional effects are slight, oxygen and the nutrient medium are satisfactorily consumed, and there is no growth in the centres of the grains.

Since one of the main purposes of immobilisation is to obtain the maximum possible concentration of the cells in the carrier, the possibility of cell growth in the carrageenan matrix is used to activate them and to accumulate the biomass.[59]

The results achieved in the preparation of biocatalysts from microbial cells immobilised in κ-carrageenan made it possible to use them for a whole series of processes.[13,17,48,60–66]

III. The use of microorganism cells immobilised in carrageenan for the synthesis of organic substances

Synthesis of L-aspartic acid. In 1969, the Tanabe Seiyaku Company (Japan) achieved the separation of the racemates of DL-aminoacids on an industrial scale using immobilised aminoacylase.[67] This was the first case of the use of immobilised enzymes. Later an attempt was made to obtain L-aspartic acid using immobilised aspartase.[68] However, the low productivity of this process led to the use of cells of *E. coli* incorporated in a polyacrylamide gel,[21] which made it possible to obtain pure L-aspartic acid in 95% yield. Taking into account the partial inactivation of the aspartase activity of the cells, the polyacrylamide matrix was replaced by κ-carrageenan.[21] In order to increase the operational stability, the immobilised cells were treated with gluaraldehyde and hexamethylenediamine. If the productivity of the cells immobilised in polyacrylamide gel is adopted as 100%, then that of the cells incorporated in κ-carrageenan was 1500%, which made it possible to initiate in 1978 the industrial manufacture of L-aspartic acid. It is of interest to note that, despite the fact that the strength of the Japanese κ-carrageenan is 650 g cm^{-2} while that of the Soviet preparation is 170 g cm^{-2}, after use for 400 h the activity of the gels immobilised in κ-carrageenan was 43 mmol g^{-1}, while that of the cells immobilised in the Soviet carrageenan was 54 mmol g^{-1}.[45]

Synthesis of L-alanine. Alanine is a valuable aminoacid required for use in medicine and the food industry. Cells of *B. dacunhae* immobilised in carrageenan were used for its continuous preparation. They were treated with glutaraldehyde,[59,63,66] and incubated at pH 4.75 and 30 °C for 1 h in order to suppress the alanine racemase and proteolytic activities. The half-inactivation time of such catalysts exceeded 280 days.

L-Alanine can be obtained more efficiently from ammonium fumarate by using in the same reactor *E. coli* cells immobilised in κ-carrageenan, which exhibit aspartase activity, and *P. dacunhae* cells with L-aspartate β-decarboxylase activity, also immobilised in κ-carrageenan.[62,64,69]

Synthesis of glutamic acid. Cells of *Corynebacterium glutamicum* ATCC 13058, immobilised in κ-carrageenan worked stably for 30 days in a flow type fermenter with a productivity of 1.08 g of glutamate per litre per hour.[61]

Synthesis of L-arginine. The reactor with *Serratia marcescens* cells immobilised in κ-carrageenan made it possible to obtain 10 mg ml^{-1} of L-arginine at pH 6.5 for a long time.[70] When pure oxygen was passed through the reactor, the immobilised cells grew five times more vigorously than the free cells.

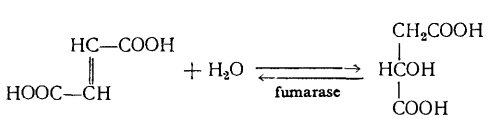
Synthesis of L-tryptophan. When *E. coli* cells with L-tryptophan synthetase activity were immobilised in polyacrylamide, alginate, and carrageenan gels, the highest activity (80% relative to the free cells) was observed for carrageenan.[71]

Synthesis of L-tyrosine. Comparison of the immobilised *Citrobacter freundii* cells with tyrosine phenol lyase activity immobilised in gelatine, agar, agar-agar, and κ-carrageenan gels indicated that the cells in κ-carrageenan were the most effective. The activity of 2–4% gels was 80% of the activity of the free cells.[72,73]

Synthesis of L-isoleucine. In order to manufacture L-isoleucine from D-threonine, a study was made of a system with growing *Serratia marcescens Ar130-1* cells immobilised in carrageenan. The reactor with the immobilised cells worked stably for 30 days with a productivity of 0.5 mg of L-isoleucine per gram of gel per hour.[14]

Synthesis of *N*-acetyl-L-methionine. *E. carotovora* cells immobilised in carrageenan cross-linked by glutaraldehyde and hexamethylenediamine catalysed the stereoselective hydrolysis of the amide of *N*-acetyl-*D*L-methionine with formation of *N*-acetyl-L-methionine and the retention of 61% of the initial activity. The optical purity was 100%.[74]

Synthesis of *L*-malic acid. In an attempt to improve the synthesis of L-malic acid, widely used in the pharmaceutical industry, from fumaric acid, the cells of *B. ammoniagenes* and *B. flavum* were immobilised in carrageenan.



If the productivity of *B. ammoniagenes* immobilised in polyacrylamide gel was adopted as 100%, then that of *B. flavum* incorporated in carrageenan was 897%.[48,75–77] It has been shown in a number of studies[51,78,79] that the thermal and operational stability of *B. flavum* cells increases sharply when they are immobilised in κ-carrageenan in the presence of polyethyleneimine and Chinese gallotannin: in the former case, the half-inactivation time for the biocatalyst increased by a factor greater than two,[79] while in the latter the increase was by a factor of 3.[78]

Manufacture of antibiotics. The cells of *Penicillium chrysogenum* immobilised in κ-carrageenan have been used to obtain penicillin *G*.[80] The cells of *Tolypocladium inflatum* synthesised cyclosporin *A*, which possesses immunodepressant properties and is used in organ transplantation.[81] The cells of *Penicillium urticae* have been used for the semicontinuous and continuous manufacture of the antibiotic patulin from glucose,[82–84] while the cells of *Xanthomonas citri*, immobilised in κ-carrageenan and treated with hexamethylenediamine and glutaraldehyde, were used to synthesise cephalexin.[85] The existence of two phases separated in time was established in the synthesis of penicillin *G* and cyclosporin *A*: cell growth (on incubation in a nutrient medium) and the formation of antibiotics.

The manufacture of ethanol. In view of the growth of the price of petroleum, there has been a growth of interest recently in the study of alcoholic fermentation by yeast immobilised in κ-carrageenan.[86–89] Problems concerning the increase in the number of cells in the gel and in the concentration of glucose and the stabilisation of gel grains with the immobilised cells have been investigated in detail.[57,58,90–92] Yeast cells immobilised in carrageenan grow more effectively than the free cells,[93] the productivity of immobilised growing cells of *Saccharomyces carlsbergensis* is three times higher than that of homogeneous cells,[58] and continuous formation of ethanol from molasses (more than 110 mg ml^{-1}) has been observed over a period of six months. The gel particles used for the manufacture of ethanol were strengthened with polyacrylamide,[54,94] by alkylenepolyamide,[53] and also by introducing tripotassium phosphate into carrageenan.[52] Metabolic inhibitors have also been introduced: dinitrophenol, azide, and arsenate.[95] Studies in which more productive microorganisms are sought are being continued.[8] When sugars were fermented by *Bacillus butacone* immobilised in carrageenan, a solution containing a butanol : acetone : ethanol = 8 : 1 : 1 mixture, which is promising for the manufacture of diesel fuel, was obtained.[96]

Synthesis of sugars. The continuous preparation of D-fructose from D-glucose has been achieved using *Streptomyces phaeochromogenes* cells immobilised in κ-carrageenan.[15] The glucose isomerase activity and the stability of the cells immobilised in carrageenan approached those for cells immobilised in polyacrylamide gel, their half-life in a column reactor amounting to 289 days.[31]

The cells of *Acetobacter* suboxydans, immobilised in a κ-carrageenan gel, produced L-sorbose in an amount of 0.2 mg per ml of the gel per hour in a stable process over a period of 15 days.[14]

The *Gluconobacter suboxydans* cells with a high alcohol dehydrogenase activity were immobilised by incorporation in a κ-carrageenan gel and were used for the biotransformation of D-arabitol into D-xylulose in 80% yield. They were activated by preliminary incubation in a nutrient medium containing D-glucose.[97]

Synthesis of acetic acid. The cells of *Acetobacter aceti* immobilised in κ-carrageenan manufactured acetic acid in a stable process for a long time at a rate of 22.5 mg per ml of the gel per hour.[98,99] *Clostridium thermoaceticum* immobilised in κ-carrageenan has been used for the same purpose.[100]

Synthesis of citric acid. *Aspergillus niger* cells immobilised in 2% carrageenan in the presence of 1% NaCl and 1% ethylenediaminetetraacetic acid, with subsequent dispersion in a mineral oil at 40 °C and treatment with polyethyleneimine or alkylenepolyamide, were used. The yield of citric acid was 5.2–5.3 g per 20 ml of the reaction mixture in 31 days.[53,101]

Synthesis of steroids and alkaloids. Steroids were one of the first substrates transformed with the aid of immobilised cells.[102] There are few instances of the employment of carrageenan for the

immobilisation of microorganisms transforming steroids and alkaloids:[103,104] these include the incorporation of *Arthrobacter globiformis* cells, which possess 3-ketosteroid Δ'-dehydrogenase activity, and the cells of *Claviceps purpurea*, which effect the biosynthesis of pharmaceutically important alkaloids: xanthoclavine, agroclavine, elymoclavine, and ergometrine. Comparison of the results with data for immobilisation in polyacrylamide gel and calcium alginate enabled the authors to conclude that they are preferable to carrageenan in the synthesis of steroids.[1]

Synthesis of vitamin B_{12}. Comparative study of the synthesis of vitamin B_{12} by cells of *Propionibacterium shermanii, P. freundenreichii subsp. shermanii ATCC 13673, Propionibacterium sp. ar I AKU 1251,* and *N_3 AKU 1253,* and *Propionibacterium sp. IAM 1714* immobilised in κ-carrageenan, calcium alginate, agar, and urethane photopolymers indicated that the cells immobilised in the urethane photopolymer have an advantage.[105]

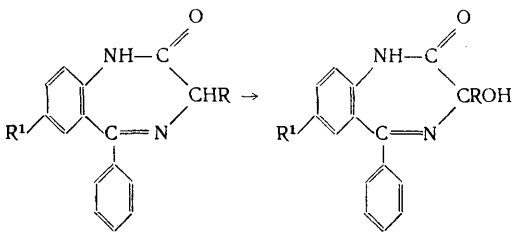
Synthesis of enzymes. The advantages of the manufacture of enzymes using immobilised cells consist in the possibility of maintaining a high concentration of cells and their rapid separation. However, the rate of diffusion of nutrients to the polymer matrix, especially of oxygen in aerobic cultures, significantly limits the growth and metabolic activity of the cells in the gel. When *Bacillus amyloliquefaciens* cells were incorporated in carrageenan, the respiratory activity and the rate of growth were suppressed to 1/2 and 1/6 respectively, but the formation of *L*-amylase was virtually similar to that by free cells.[106]

Synthesis of dihydroxyacetone. Dihydroxyacetone, which is used in the cosmetic and food industry, was synthesised from glycerol by *Gluconobacter melangenes* cells immoblised in κ-carrageenan.[107]

Synthesis of butane-2,3-diol. The cells of *Enterobacter aerogenes* immobilised in κ-carrageenan manufactured butane-2,3-diol stably over a period of ten days. On activation by incubation in a nutrient medium, the cells multiplied by a factor of 200.[108]

Reduction of nitro-compounds. The nitroreductase activity of *E. coli* cells immobilised in phyllophorin from the broad-jointed form of phyllophora and in carrageenan from spherical phyllophora is higher than that of cells immobilised in κ-carrageenan. The maximum retention of nitroreductase activity is then observed for the cells: carrageenan gel = 1:10 weight ratio. The study of the granulation conditions showed that the optimum granulation is in toluene at 0–4 °C. The gel grains with immobilised cells having a high nitroreductase activity are strengthened in 0.3–0.4 M KCl solutions. The study of the modification of the immobilised preparations by amines (ammonia, hexamethylenediamine, hydrazine hydrate, diethylamine, and triethylamine), glutaraldehyde, and titanium tetrachloride showed that the nitroreductase activity of the preparations treated with titanium tetrachloride is at the level of the unmodified preparations, while on treatment with diethylamine and triethylamine, it increases to 122 and 145% respectively. The reduction of nitro-derivatives of benzo-2,1,3-thiadiazoles and 1,4-benzodiazepin-2-ones as well as substituted nitrobenzenes with formation of the corresponding amines under column conditions has been achieved with the aid of the biocatalysts obtained.[109,110]

Synthesis of 3-hydroxy-1,2-dihydro-3*H*-1,4-benzodiazepin-2-ones. It has been shown[111] that the transformation of 1,2-dihydro-3*H*-1,4-benzodiazepin-2-ones by actinomycetes immobilised in carrageenan results in the formation, in 65% yield relative to the activity of the free cells, of optically active (+)3-hydroxy-derivatives having a more pronounced activity in their antagonism to corazole and in potentiating hexenal sleep compared with the racemate.



The achievement of this process makes it possible to obtain the corresponding 3-hydroxy-derivatives in one stage instead of the six stages required in the chemical method of synthesis.

Purification of waste water. The cells of *Clostridium pasteurianum* and *Alcaligenes eutropis*, catalysing the reaction $HT + H_2O \rightleftarrows H_2 + HTO$, were immobilised in calcium alginate and κ-carrageenan in order to remove tritium from water contaminated by radioactive impurities (for example, from the cooling systems of atomic power stations).[112] In terms of its catalytic activity, 10 g of cells immobilised in carrageenan is equivalent to 1 g of a platinum catalyst, but, in contrast to the latter, the former catalysts are cheap, can be readily obtained in a large amount, and are active in the liquid phase.

The reduction of the acidity of materials for the production of wine. It has been shown that the cells of *Leuconostoc oenos* immobilised in carrageenan effect the 100% transformation of L-malic acid into L-lactic acid in the treatment designed to reduce the acidity of materials for wine making. Thus, summarising the data presented above, one may conclude that microorganism cells immobilised in carrageenan are likely to be useful in the synthesis of organic compounds.

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In conclusion, the authors express the hope that this review will serve as a starting point for further study of the possibilities of using immobilised microorganism cells in organic synthesis, which will help create new biocatalysts for practical employment. Here attention should be concentrated on the study of Soviet produced carrageenan and its applicability in the immobilisation of cells. Evidently, more detailed investigation of the immobilisation and of the mechanism of gel formation will permit a deeper understanding of the nature of the intermolecular interactions in polysaccharide complexes and of the causes of the increased stability of microorganism cells immobilised in carrageenan and will help to develop more effective methods of synthesis of organic substances for the needs of industry, agriculture, and medicine.

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Organic and molecular ferromagnetics: advances and problems

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ABSTRACT. The possible ways of creating organic and molecular ferromagnetics are analysed and the principles of the molecular design of these magnetic substances are examined. Comparison of the theoretical predictions with the experimental results permits certain conclusions and predictions as to whether different ways of creating molecular ferromagnetics are realistic.

The bibliography includes 68 references.

Contents

I. Introduction 307
II. Multispin and high-spin molecules 307
III. The ideas and theoretical foundations of "organic" ferromagnetism 310
IV. Molecular crystals 312
V. Organic polymers 314
VI. Organometallic polymers 316
VII. Conclusion 317

I. Introduction

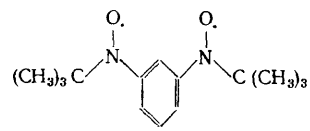
All the known ferromagnetics are made up of metal atoms with unfilled *d* or *f* electron shells, i.e. on the basis of the spin magnetism of the inner *d* and *f* electrons. The question arises whether it is possible to create ferromagnetics on the basis of *s* and *p* electrons. Experiment shows that alkali and alkaline earth metals, in the atoms of which the spin is due to the outer *s* or *p* electrons, are non-magnetic. Organic radicals with outer *p* electrons also lose their paramagnetism at low temperatures and become non-magnetic. Solid oxygen is diamagnetic, although the oxygen molecule is paramagnetic. These phenomena have a common cause: for all the atoms with *d* and *f* electrons, the exchange interaction (i.e. that part of the Coulombic, electrostatic interaction of electrons which depends on their spin) is positive and arranges the electron spins on the neighbouring atoms in parallel (in a ferromagnetic manner); for atoms with *s* and *p* electrons, the interatomic (or intermolecular) exchange interaction is negative and gives rise to an antiparallel arrangement of the electron spins on the neighbouring atoms or molecules (in an antiferromagnetic manner).

The problem of "organic" ferromagnetism is how to obviate this difficulty and how to find ways and procedures whereby a ferromagnetic arrangement of electrons in organic paramagnetic molecules, i.e. in molecules with *s* or *p* unpaired electrons, can be achieved. An organic ferromagnetic is understood to be a magnetic material made up of purely organic paramagnetic molecules; this is a special albeit important case of a molecular ferromagnetic in which paramagnetic molecules may contain metal atoms (for example, organometallic molecules).

In order to create an organic or molecular ferromagnetic, two main conditions are essential. Firstly, a building material is needed, namely organic multispin paramagnetic molecules (high-spin molecules are best) with a high density of oriented spins in order to ensure an appreciable magnetisation. Secondly, a procedure is needed (and this is the main problem) for organising these molecules in the crystal or in an amorphous body in such a way that a ferromagnetic arrangement of the spins is achieved.

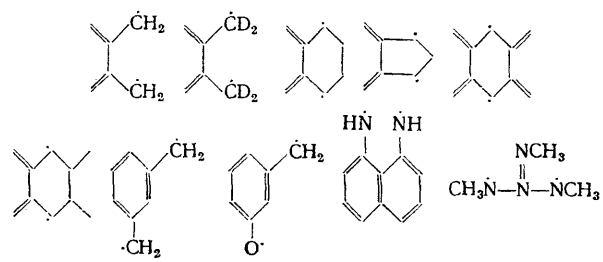
II. Multispin and high-spin molecules

The construction of high-spin molecules is the first part of the problem and here most progress has been achieved. Independently of organic ferromagnetics and long before their appearance, major advances were made in the chemistry and physics of stable organic radicals and an enormous number of such radicals with a wide variety of structures belonging to various chemical classes were synthesised.[1] Many stable biradicals were created on their basis, most of them being of the low-spin type ($S = 0$, singlet ground state). However, among them there are many high-spin species ($S = 1$, triplet ground state), for example:



as well as certain bisphenoxyls, bisverdazyls, etc. (for further details, see Buchachenko and Vasserman[1]).

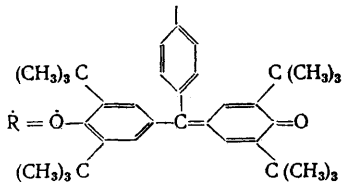
In connection with organoferromagnetics, interest in these biradicals was revived from new standpoints: the question arose how the unpaired electrons within the molecule interact, under what conditions is their exchange interaction positive and arranges the spin in a ferromagnetic manner (triplet ground state), and when is it negative (zero overall spin, singlet ground state). Many simplest biradicals of the type



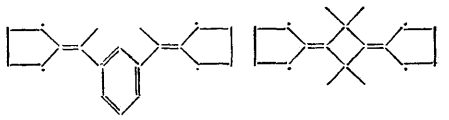
were synthesised (they were obtained at low temperatures mainly by the photolysis of the corresponding azo-compounds and other precursors). It has been demonstrated convincingly (by EPR) that

they all have the spin $S = 1$ and a triplet ground state and that the dipole interaction of their electrons amounts to $D \simeq 0.01-0.03$ cm^{-1}.[2,3] We may note that it has been frequently predicted quantum-chemically that these biradicals have singlet ground states and the idea actually arose that Hund's rule breaks down for such π-conjugated non-Kekulé structures. However, experiment confirmed the presence of the triplet state—in agreement with the simplest valence bond scheme.

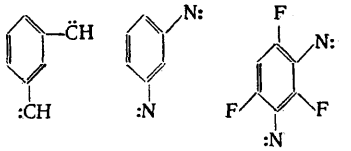
High-spin molecules based on polyradicals, carbenes, and polycarbenes are also known. For example, the stable tetraphenoxyl $C\dot{R}_4$, i.e.



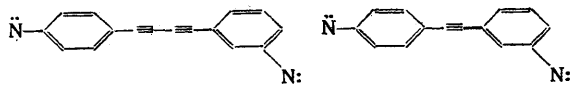
has a quintet ground state ($S = 2$, exchange interaction with $J \simeq 600$ MHz);[4] the tetraradicals



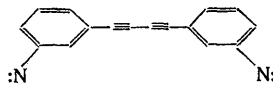
also have a quintet ground state ($S = 2$).[5] In the bicarbenes and binitrenes



the exchange interaction of the electrons is positive and stabilises the high-spin (quintet) state.[3] In binitrenes, compounds with acetylenic and diacetylenic bridges of the *para—meta* type (one nitrogen atom is in the *para*-position and the other is in the *meta*-position relative to the substituent), i.e.

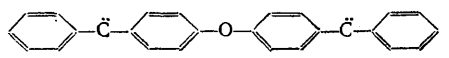


the high-spin state with $S = 2$ is also stabilised, but if the combination of the nitrenes is of the *meta—meta* type, i.e.

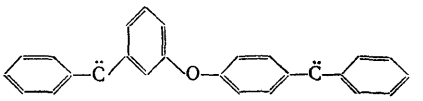


the low-spin singlet state (with $S = 0$) is stabilised.[6] (One can predict that a compound of the *para—para* type will also stabilise the singlet state.)

By combining carbene systems, it is likewise possible to obtain both high-spin and low-spin molecules. Thus the combination of two diphenylcarbenes (each of these fragments is in a high-spin triplet state) of the *para—para* type, i.e.



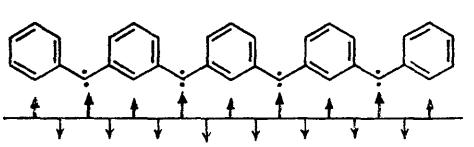
stabilises the low-spin singlet state ($S = 0$), i.e. the exchange interaction of the electrons arranges the electron spins within the molecule in an antiferromagnetic manner. A combination of the *meta—meta* type stabilises the low-spin state, but a combination of the *meta—para* type, i.e.



stabilises the high-spin ($S = 2$) quintet state of this dicarbene.[7]

We shall now turn to the problem when and under what conditions and in what systems is the exchange interaction positive and stabilises the high-spin electronic state of the molecule and when is it negative and even a molecule with a large number of unpaired electrons is in a low-spin state; in the former case, a ferromagnetic arrangement of all the spins in the molecule takes place, while in the latter case an antiferromagnetic arrangement obtains. It would seem that it is possible to count on an exact answer from the rigorous quantum chemistry of the molecule, but theory frequently falls out of step (we have seen an example above), the reason being that spin molecules are systems with open shells for which an exact calculation is unreliable (particularly when one is dealing with small differences between the energies of spin states). There is, however, a simple way of predicting the sign of the exchange interaction and the spin state based on a simple valence bond scheme and on the ideas of spin delocalisation and spin polarisation; as a result of delocalisation, the spin is distributed throughout the molecule and spin polarisation induces a negative spin density at certain points within the molecule, i.e. the local spin at these points is oriented against the total spin. (An example is provided by the allyl radical $\dot{C}H_2 - CH = CH_2$ in which the spin is distributed on the terminal carbon atoms and its density is positive—~0.45 on each; however, on the central atom the spin polarisation induces a negative spin density of about −0.01.) If the spin densities of both electrons in a two-spin system (for example in a π-electron biradical) alternate rigorously as regards sign (in other words, the two spins are separated by a negative spin density), a triplet state obtains, but if the distribution of spins in the molecule results in the appearance of direct spin contacts (i.e. there are no regions of negative spin density between them), the low-spin state is stabilised.

We shall demonstrate this rule in relation to the polycarbene synthesised by Iwamura and co-workers:[8,9]

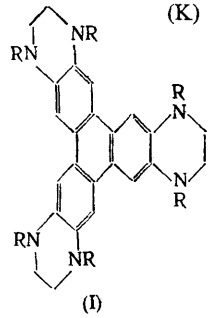


Five phenyl rings are linked by carbene fragments at the *meta*-positions. The signs of the spin densities are indicated below: the bold arrows denote positively oriented spins and the thin arrows denote negatively oriented spins. Evidently the signs of the local spins alternate rigorously: the contacts between positive spins are formed solely via atoms with negative spins. Clearly a high-spin state of this carbene should be achieved. Indeed the spin of this molecule is $S = 4$ and the ground state has the nonet multiplicity ($2S + 1 = 9$)[8] and all 8 unpaired electrons are arranged in a ferromagnetic manner.

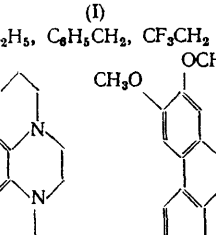
Using this rule, it is easy to demonstrate that the binitrenes or bicarbenes discussed above are high-spin species when they are combined via a *meta—para* junction but are low-spin species if the

combination of the nitrene or carbene groups is of the *meta—meta* or *para—para* type. These predictions agree with experiment. It is easy to extend these rules to any case of polyconjugated multispin systems and to predict when the multispin system will be in a high-spin state and when it will be in a low-spin state. In other words, it is possible to show when the multispin molecule will be "ferromagnetic" and when it will be antiferromagnetic (strictly speaking these concepts are macroscopic and refer to a crystal or an amorphous body, but we shall sometimes apply them also to molecules). These features and rules are useful in predicting the synthesis of high-spin molecules as potential precursors of organic ferromagnetics.

Among the high-spin molecules, charged species are known. Thus the cyclopentadienyl and pentachlorocyclodienyl cations are triplet species,[10,11] although their stability is low. On the other hand, the pentaphenylcyclopentadienyl cation has a singlet ground state.[12] Interest in organic ferromagnetics has stimulated the search for and the synthesis of stable high-spin cations. The hexachlorobenzene cation is known to be in a triplet state but is unstable.[13] Breslow and co-workers[14,15] synthesised aromatic hexazo-molecules of the type

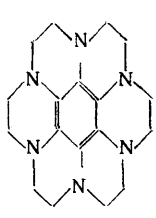


(K)

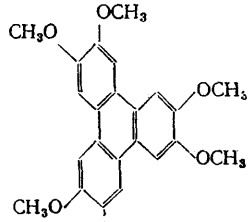


(I)

R=C_2H_5, $C_6H_5CH_2$, CF_3CH_2 etc.

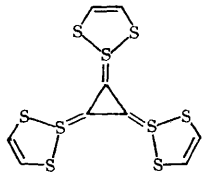


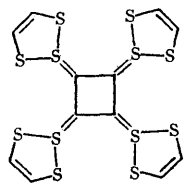
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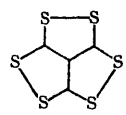


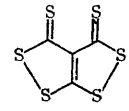
(III)

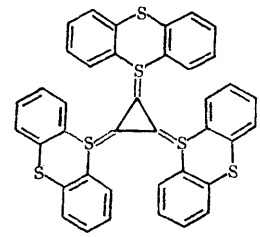
whose dications are stable triplet species. Compound (I, R = C_2H_5) has been designated[14,15] by the abbreviation HET (hexaethyltriphenylene) and compound (II) has been designated by HOC (we shall make use of these abbreviations below). Chiang et al.[16] synthesised hexamethoxytriphenylene (HMT) (III), whose dication is also a stable triplet species. Readily oxidised sulphur-containing molecules of the type





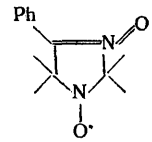






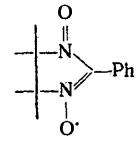
have been synthesised and it is expected (and the first confirmations have already been obtained) that their dications are high-spin triplet species, which may be suitable for the creation of organic ferromagnetics.[17,18]

Mixed organometallic high-spin complexes have already been synthesised. Thus in the complex $3Cu(hfacac)_2.2L$, where hfacac = perfluorinated acetylacetonate and L = nitroxyl, with two complex-forming groups, i.e.



the exchange interaction of the electrons of the metal ion and the ligand is positive (~ 12 cm^{-1}) and stabilises the high-spin state of the complex.[19]

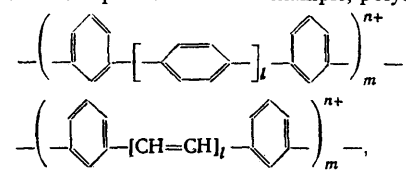
In the complex of the nitroxyl radical



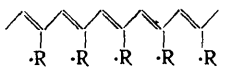
with $Mn(hfacac)_2$, six Mn^{2+} ions and six ligand radicals form a ring with ferromagnetic intramolecular interaction of all the unpaired electrons; it stabilises the high-spin state of the complex with the total spin $S = 6(5/2) + 6(1/2) = 18$.[20,21] In the complex $[Cr_4S(O_2CCH_3)_8(H_2O)_4]_2.H_2O$, the Cr_4S cluster has a spin $S = 6$ in the ground state.[22] In the complexes $Mn_{12}O_{12}(O_2CCPh)_{16}(H_2O)_4$ and $Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4$, the cluster nucleus contains the Mn_4^{4+} and Mn_8^{3+} ions with a positive exchange interaction, which stabilises the high-spin state of the cluster with a spin $S = 14$.[23]

Finally, macromolecules (linear or two-dimensional networks) with a high density of paramagnetic centres are multispin species with the largest number of spins. Spin-labelled polymers with a high concentration of paramagnetic labels—nitroxyl and verdazyl radicals (in the limit one paramagnetic fragment per monomer unit)—have been synthesised. These polymers and their magnetic properties are described below in Section V; organometallic multispin macromolecules and the magnetic properties of the corresponding polymers are discussed in Section VI.

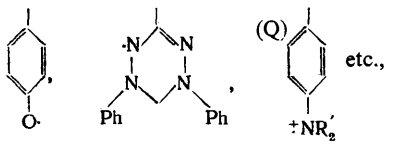
For the purpose of synthesis, hypothetical structures have been proposed for linear multispin molecules in which a "ferromagnetic" exchange interaction of the spins and the stabilisation of the high-spin state are expected.[24–26] For example, polycations of the type



in which the blocks comprising poly-*p*-phenylenes or polyenes are joined via phenyl rings, should be high-spin species. The polyene macromolecules



where R are the radical fragments



should also be ferromagnetic (according to the predictions formulated above). On the basis of the same principle, it is possible to suggest a series of other "ferromagnetic" macromolecules for synthesis.

Mataga[27] was the first to propose the hypothetical structures of high-spin planar two-dimensional hydrocarbons made up of triplet diphenylcarbenes combined into a single conjugated system via the *meta*-positions in the phenyl rings (actually the polycarbene with a spin $S = 4$, examined above, is a fragment of such a structure and has been synthesised in accordance with Mataga's principle). Another two-dimensional structure, which he also proposed, is based on the triphenylmethyl radical as the main structural element; the interaction of unpaired electrons is effected via the *meta*-positions in the phenyl rings. Mataga regarded both systems as potential precursors of organic ferromagnetics.[27]

A number of interesting linear and two-dimensional conjugated systems have been proposed by Ovchinnikov;[24] they include a hypothetical boron-substituted graphite—a high-spin system which is a possible precursor of a ferromagnetic. The same worker proposed a general theory and formulated a simple rule which permits the prediction of the spin of such polyconjugated high-spin molecules. The experimental data concerning the construction of organic ferromagnetic polymers on the basis of multispin molecules will be examined below (see Section V).

III. The ideas and theoretical foundations of "organic" ferromagnetism

In organic spin molecules, the unpaired electrons populate the highest of the occupied molecular orbitals and are localised on the "surface" of electron shells. The exchange intermolecular interaction of unpaired electrons is therefore negative and antiferromagnetic, orienting the spins of neighbouring, even high-spin molecules in opposition to one another. The key problem in "organic" ferromagnetism is how to overcome this difficulty; the attainment of ferromagnetism through antiferromagnetic interactions—this is the paradoxical formulation of the problem.

Several ideas for the resolution of this paradox have been proposed and we shall now consider them. The first was formulated as early as 1963 by McConnel.[28]

As we have already seen above, two mechanisms are significant in the propagation of the spin in the molecule—spin delocalisation and spin polarisation. The interplay of these mechanisms make the distribution of the unpaired electrons in a spin molecule non-uniform not only in magnitude but also as regards sign: at certain points within the molecule, the spin density is negative, i.e. a local (partial) spin is oriented in opposition to the total spin of the unpaired electron. The regions of positive spin density in the molecule frequently alternate with regions of negative spin density. Suppose that in a crystal or glass the spin molecules can be organised in a remarkable manner such that the regions of positive spin density of one molecule are in contact with the regions of negative spin density of another and this order is retained throughout the given volume. It is readily seen that in such a system the negative intermolecular (interspin) exchange generates two spin subsystems: positive spin densities oriented on one side and negative spin densities oriented on the opposite side (as in a ferromagnetic). However, the positive spin densities are much greater than the negative spin densities and the overall spin corresponds to a ferromagnetic arrangement, the substance becoming an organic ferromagnetic.

We shall refer to this route to ferromagnetics as the McConnell mechanism and the regions of intermolecular contact in which the positive spin densities of one molecule are combined with the negative spin densities of another will be referred to as the McConnell islands. There is direct evidence for this mechanism—both theoretical and experimental. A calculation has been carried out for the allyl + methyl radical pair in terms of the geometry illustrated in Fig. 1.[29] In case *a*, the methyl radical approaches one of the terminal carbon atoms of the allyl radical (the π-electron spin density on these atoms is positive and amounts to ~0.49 on each), while in case *b* the methyl radical approaches the central atom (the spin density on this atom is negative, amounting to −0.01). The McConnell island arises only in case *b*—this is the region where the positive spin density of the methyl radical is in contact with the negative density of the central atom of the allyl radical.

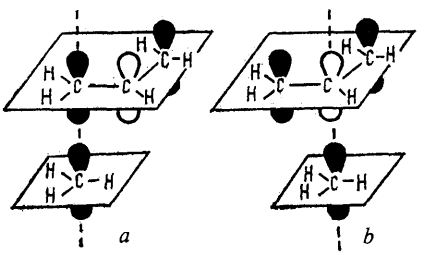


Figure 1. Schematic illustration of the disposition of the partners in the allyl + methyl radical pair: (*a*) the methyl group approaches the terminal carbon atom of the allyl group, where the spin density is positive; (*b*) the methyl group approaches the central atom of the allyl group with a negative spin density.[29]

Fig. 2 presents the dependence of the exchange interaction on the distance between the radicals. In case *a*, the exchange interaction is negative, there is a singlet ground state, and the orientation of the spins in the pair is antiferromagnetic. In case *b* (where there is a McConnell island), the exchange interaction is positive and stabilises the high-spin triplet state, while the orientation of the spins in the pair corresponds to ferromagnetism. The simplicity of the system for which the calculation has been made and the identity of the approximations used in the calculations in both versions, *a* and *b*, as well as the independence of the principal results of the method of calculation ensure the reliability of the result.

Another piece of evidence is experimental.[30]

Substituents (triplet phenylcarbenes) were introduced into the phenyl rings of paracyclophanes fixed in space by chemical—CH_2CH_2—bridges in different positions within the ring: pseudo-*ortho*- (Fig. 3*a*), pseudo-*meta*- (Fig. 3*b*), and pseudo-*para*- (Fig. 3*c*). It is readily seen that, when the unpaired π-electron migrates from the carbene to the phenyl ring of the cyclophane, the distribution of its spin density in the pseudo-*ortho*- and pseudo-*para*-structures creates McConnell islands—spin densities of one sign in one phenyl ring of cyclophane are located opposite the spin densities of the reverse sign in another ring. In the pseudo-*meta*-structure, there are no McConnell islands—spin densities of the same sign are in contact. In exact correspondence to this property, the arrangement of spins in the pseudo-*ortho*- and pseudo-*para*-structures is ferromagnetic (quintet ground state, $S = 2$), while in the pseudo-*meta*-structure it is antiferromagnetic (singlet ground state). These results were also reproduced for cyclophanes whose phenyl rings are fixed in space by—$CH_2CH_2CH_2$—bridges.[6]

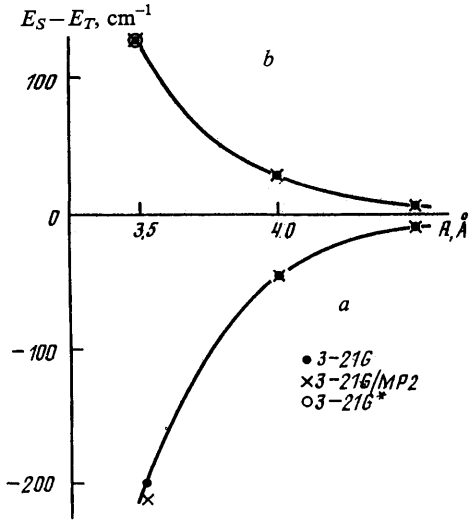


Figure 2. The exchange interaction (singlet–triplet splitting) in the allyl + methyl radical pair as a function of the distance R between the partners for the two types of their mutual approach (*a* and *b*). Circles—results of the calculation in terms of three different approximations; continuous lines—their exponential representations.[29]

These two simple and elegant proofs reliably justify the McConnell mechanism of the route to organic ferromagnetics.

The second idea was also put forward by McConnell in 1967[31] and referred to the possible ferromagnetism of a special class of compounds—the radical-ion salts of the type ...$D^+A^-D^+A^-D^+A^-$... constructed as quasi-one-dimensional spin chains of the donor radical-cations D^+ alternating rigorously with the acceptor radical-anions A^-. It was suggested that virtual excited states of the D^+A^- pair may exist, stabilising its high-spin triplet state and ensuring a ferromagnetic arrangement of the spins in the quasi-one-dimensional chain. An admixture of such excited states can arise as a result of the virtual forward charge transfer ($D^+ + A^- \rightarrow D^{2+} + A^{2-}$), the reverse charge transfer ($D^+ + A^- \rightarrow D^0 + A^0$), or a disproportionating charge transfer ($D^+ + D^+ \rightarrow D^{2+} + D^0$). If any one of the charge transfer states (D^{2+}, D^0, or A^{2-}, A^0) is singlet, the singlet spin state of the D^+A^- pair, to which corresponds an antiferromagnetic arrangement of the spins in the chain, is established. If even one of the species D^{2+}, D^0 or A^{2-}, A^0 is a high-spin triplet molecule (and this is its ground state), then the virtual charge transfer will stabilise the high-spin state of the D^+A^- pair and will give rise to a ferromagnetic arrangement of the spin chain.

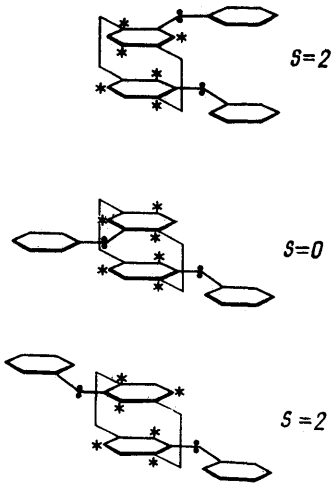


Figure 3. The structures of paracyclophane dicarbenes—pseudo-*ortho* ($S = 2$), pseudo-*meta* ($S = 0$), and pseudo-*para* ($S = 2$).[30]

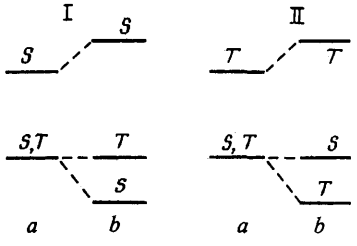


Figure 4. The energy levels of the D^+A^- pair without taking into account the virtual charge transfer (*a*) and the change in the energy levels when account is taken of the virtual charge transfer (*b*). Case I corresponds to the stabilisation of the singlet state of the pair and case II corresponds to the stabilisation of the triplet state.

The energy level schemes for these versions are illustrated in Fig. 4. The normal state of the D^+A^- pair is degenerate (the difference between the energies of the singlet S and the triplet T may be neglected), but the virtual charge transfer in the excited state of

the pair reduces the energy of the singlet (if the transfer takes place with participation of the singlet state of one of the D^{2+}, A^{2-}, D^0, and A^0 species) and of the triplet (if even one of the D^{2+}, A^{2-}, D^0, and A^0 species has a high-spin triplet ground state). The schemes in Figs. 4*a* and 4*b* correspond to the first and second versions respectively. The reduction of energy as a result of the admixture of the excited state of the pair (virtual charge transfer) can be estimated in terms of the perturbation theory; it is a quantity of the order of magnitude of $t^2/\Delta E$, where ΔE is the excitation energy of the pair and t is the charge transfer integral.

This simple idea was specified in detail by Torrance et al.,[32] was expanded by Breslow and Le Page,[15] and was generalised by Miller and Epstein.[33]

In order to generate ferromagnetism by means of this mechanism, it is necessary that one of the partners (but not both) should have a degenerate and partly occupied molecular orbital; an appreciable charge transfer is needed, i.e. an appreciable admixture of the excited state of the D^+A^- pair, in order to stabilise its ferromagnetic and antiferromagnetic states; the molecules must be highly symmetrical without any structural or electronic defects (of the type of the Jahn–Teller effect), which remove the degeneracy already in the ground state.

There is no direct evidence for this mechanism of the generation of ferromagnetism, although most of the studies (both experimental and theoretical) have been devoted to the development of precisely this field. Highly symmetrical molecules, producing excellent readily crystallisable radical-ion salts, have been specially synthesised in conformity with this mechanism; furthermore, among them are there also those which produce doubly charged high-spin cations ideally corresponding to the conditions for charge transfer and the stabilisation of the ferromagnetic state [of the type $(HET)^{2+}$ and $(HOC)^{2+}$; see Section II]. However, ferromagnetics were never obtained (with the exception of metallocene salts—this will be discussed later in Section IV). Here one should recall that, regardless of the search for ferromagnetism, an enormous number of radical-ion salts (including organic superconductors) are known, but they all become antiferromagnetic at low temperatures (like other organic paramagnetic materials). One-dimensional spin chains are known to be unstable in such salts (Peierls instability): the chain breaks up into pairs with a strong interaction within the pair and a weak interaction between the pairs. This suppresses the virtual charge transfer (and yet ferromagnetism requires a collective charge transfer throughout the sequence of ions in the chain, since otherwise a complete arrangement of all the spins is not achieved). The Peierls instability is in fact the cause of the conversion of highly conducting radical-ion supports (organic metals) into dielectrics and can prevent the possible transition of the chain to the ferromagnetic state. Incidentally, the theory of spin waves in radical-ion chains has been thoroughly developed and predicts the antiferromagnetism of these chains (in agreement with experiment).

The third idea[34] is the cocrystallisation of low-spin and high-spin molecules (for example monoradicals and biradicals with spins of 1/2 and 1). If their chemical structures are almost identical, one may expect a regular alternation of the two types of molecules in the crystal. Negative intermolecular exchange arranges the spins of neighbouring species in opposition and generates two spin sublattices: the spins of molecules of one kind are oriented in one direction and those of molecules of the other kind are oriented in the opposite direction. The overall ferrimagnetic arrangement of the spins is illustrated schematically in the two-dimensional version in Fig. 5. This idea was confirmed experimentally in relation to organic metallic polymers (see Section VI); it gives rise to a simple route to the ferromagnetic arrangement of multispin molecules (at any rate it is now not more complex than the arrangement of the McConnell islands).

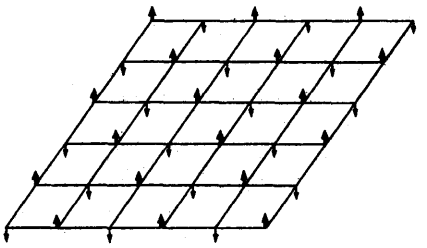


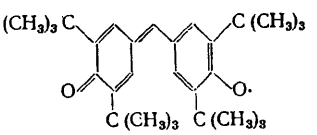
Figure 5. Two-dimensional ferrimagnetic spin lattice.

We shall now proceed to the analysis of experimental studies carried out in connection with the search for organic ferromagnetics.

IV. Molecular crystals

The magnetic properties of stable organic radicals of different classes and their relation with the structure of the crystals have been described systematically and surveyed.[35] Their common property is paramagnetism which obeys the Curie–Weiss temperature law with a negative Curie–Weiss point corresponding to the antiferromagnetic interaction of the spins. Indeed, at low temperatures the crystalline radicals become antiferromagnetics. Compression of the crystals does not alter the negative sign of the exchange interaction and merely enhances the antiferromagnetism, shifting the Curie–Weiss point to higher temperatures.[36]

There are several exceptions to this general rule, among which only two are trustworthy. This concerns a phenoxyl radical (the galvinoxyl) radical, i.e.



and its deuterio-analogue (the central CH group has been replaced by the CD group).[37,38] The high-temperature crystalline phase of the galvinoxyl ($T \geqslant 85$ K) is paramagnetic but shows signs of ferromagnetism (a positive Curie–Weiss temperature of 19 K).[38] Below 85 K, there is a phase transition and there is a new low-temperature phase, this time antiferromagnetic. In mixed crystals with the added phenolic precursor of galvinoxyl (its crystallisation is of the same type as that of its radical), the phase transition is suppressed and the higher the content of the phenol in the crystal the lower the temperature at which the high-temperature ferromagnetic phase is retained.[39–41]

In mixed crystals of galvinoxyl with its phenol, direct evidence was also obtained for the ferromagnetic interaction between the radicals in the high-temperature ferromagnetic phase. For high

dilutions with the phenol [low (1–10%) contents of the radical], EPR signals characteristic of triplet states (including forbidden transitions at $g = 4$) were observed in the mixed crystals.[41] It follows from the temperature variation of the intensity of these signals that there is a triplet ground state and the latter was referred to a radical pair with a positive, ferromagnetic interaction of the spins $J \simeq 1.5 \pm 0.7$ meV (approximately 30 cal mol^{-1}).

For high contents of the radical in the mixed crystals, triplets, quadruplets, etc., i.e. radical clusters, appear together with the isolated radical pairs. There is of course a distribution with respect to the sizes of these clusters, which is generated in the lattice by the insertion of phenol molecules between the radicals. It has actually been possible to estimate the sizes of the clusters.[41] Thus in a mixed crystal with ~20% of phenol the dependence of the magnetisation $M(H)$ on the magnetic field is described satisfactorily by the Brillouin function $B_J(x)$:

$$M(H) = M_S B_J(x), \text{ where } x = Jg\mu_B H/kT,$$

whence it was found that the average size of the ferromagnetic cluster corresponds to six radicals; its spin is $S = 3$ and it has a septet ground state ($2S + 1 = 7$).[40]

Thus the high-temperature phase of galvinoxyl is ferromagnetic not only as regards macroscopic features (positive Curie–Weiss temperature) but also as regards molecular features: the exchange interaction in the radical pairs and in the radical clusters is also positive and ferromagnetic, stabilising the high-spin states of the pairs and clusters. This means that the high-temperature phase of galvinoxyl can be regarded as the first organic ferromagnetic.

The low-temperature phase of this radical is antiferromagnetic—this follows also from the negative Curie–Weiss temperature and from EPR data. EPR signals corresponding to triplet states were also found in this phase, but it follows from the temperature variation of their intensity that these triplets are thermally excited and that there is a low-spin singlet ground state corresponding to the antiferromagnetism of this phase. The exchange interaction of the radicals in the antiferromagnetic phase is fairly intense (about 45 meV).[41]

The question arises of the cause of the anomalous ferromagnetism of galvinoxyl among radicals. The crystal structure of its high-temperature ferromagnetic phase is illustrated in Fig. 6.[42] The lattice is monoclinic and there are four molecules in the unit cell. The planar molecules are arranged in layers; one-dimensional chains of radicals are formed along the c axis of the crystal. They are "skewed" in such a way that opposite the $-CH=$ groups of one radical there are the phenyl rings and oxygen atoms of another radical at a very short distance. In other words, the regions with negative spin density (in galvinoxyl, this is the $-CH=$ group) are in contact with regions where the spin density is predominantly positive (oxygen atoms and phenyl rings). These are McConnell islands and are apparently the cause of the ferromagnetic arrangement of the spins[43] in the high-temperature phase of galvinoxyl.

Naturally, this is only a hypothesis, but it is difficult to find an alternative. It will be extremely important to establish the crystal structure of the low-temperature, antiferromagnetic phase of galvinoxyl. If it is such that there are no McConnell islands, this will be evidence in support of the proposed explanation of the ferromagnetism and even in support of the entire concept of McConnell islands.

We shall now deal with the search for other molecular ferromagnetics. As already mentioned (see Section II), polycarbene has a high-spin molecule but the hopes that after the accumulation of such molecules at sufficient concentrations signs of a ferromagnetic behaviour of the system would appear proved vain.[7]

When polycarbenes were generated in frozen glasses, in a host (benzophenone) single crystal in which the molecules of polyazide (a precursor of polycarbene) were incorporated, and also in polyazide crystals, the accumulation of polycarbenes was always accompanied by the appearance of signs of antiferromagnetic behavoiur (negative Curie–Weiss temperature.[8] This means that the intermolecular exchange interaction of even the high-spin molecules is antiferromagnetic (as in solid oxygen).

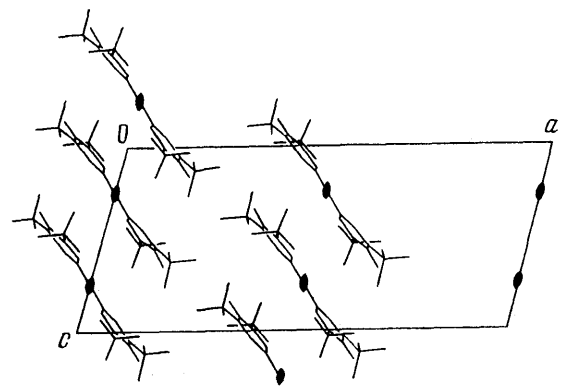


Figure 6. The crystal lattice of galvinoxyl.[42]

As already mentioned above, the search is directed principally towards the synthesis of radical-ion salts in which the conditions for the virtual charge transfer, stabilising the ferromagnetic arrangement of the spins, are achieved (see Section III). Among the large number of such salts of the type $D^{+\cdot}A^{-}$, where the donor D consists of HOC, HET, and HME molecules (see Section II), while the acceptor A consists of TCNQ, TCNE, $TCNQF_4$, and hexacyanotrimethylenecyclopropane molecules, no signs of ferromagnetism were observed; on the contrary, all the salts were clearly antiferromagnetic.[15,16,32] However, all the conditions satisfying McConnell's second idea are in fact brilliantly fulfilled in precisely these salts—they crystallise as ideally ordered alternating chains of cations and anions and the virtual charge transfer $D^{+\cdot} + A^{-\cdot} \rightarrow D^{2+} + A^{2-}$ gives rise to the doubly charged cation D^{2+} in the triplet, high-spin state (see Section II) and it should therefore stabilise the ferromagnetic state of these salts. Thus the idea of the virtual charge transfer as a means of ensuring the ferromagnetism of radical-ion salts has not so far been justified.

A remarkable exception to this series of failures is certain radical-ion salts of the decamethylferrocenium radical-cation $[Fe(C_5Me_5)_2]^{+\cdot}$ with the radical-anions $(TCNE)^{-\cdot}$, $(TCNQ)^{-\cdot}$, and $[C_4(CN)_6]^{-\cdot}$. They have been synthesised and investigated by Miller, Epstein, Reiff, and co-workers[44–49] and although they contain an iron atom, they should be regarded as true molecular ferromagnetics because their ferromagnetism is associated with the unpaired electron in the highest occupied molecular orbitals of the ferrocenium ion.

The above ferrocenium salts form ideal one-dimensional spin chains of alternating cations and anions. The ferromagnetic properties are manifested most strikingly by the salt

$[Fe(C_5Me_5)_2]^+(TCNE)^-$: the Curie–Weiss temperature is 30 K, the saturation magnetisation of the polycrystalline material at 2 K in magnetic fields $H > 300$ Oe is 11000 e.m.u. mol^{-1} (this is comparable to the magnetisation of metallic iron under normal conditions), and sextets characteristic of a ferromagnetic appear in the ^{57}Fe Mössbauer spectra near 9 K.[45] Spontaneous magnetisation ($m \simeq 2000$ e.m.u. mol^{-1}) appears in a zero magnetic field at $T < 4.5$ K. In a single crystal, when the magnetic field is oriented along the axis of the one-dimensional arrangement of cations and anions, the saturation magnetisation is 16000 e.m.u. mol^{-1}; this is greater by 36% than for metallic iron (when calculated per atom) and agrees with the theoretical magnetic saturation moment in the ferromagnetic arrangement of the spins of the cation ($S = 1/2$, $g = 4$) and the anion ($S = 1.2$, $g = 2$). There is also a hysteresis loop with a coercive force of 30 Oe at 4.2 K and 1000 Oe at 2.0 K.[47]

It follows from the temperature variation of the magnetic susceptibility χ, the magnetisation M, and the field dependence $M(H)$ that above 16 K the magnetic properties are best described by the one-dimensional Heisenberg exchange model with $J = 19$ cm^{-1}, while at $T < 16$ K the substance is closer to a three-dimensional ferromagnetic.

The magnetisation of the salt $[Fe(C_5Me_5)_2]^+(TCNQ)^-$ in fields $H < 1.6$ kOe is characteristic of an antiferromagnetic, but for $H > 1.6$ kOe it increases abruptly and rapidly attains saturation, which is characteristic of a ferromagnetic. This is a feature of a metamagnetic—a layered magnetic (of the type of $FeCl_2$) in which the intensity of the exchange interaction within the layer exceeds that of the exchange interaction between the layers. A number of inorganic metamagnetics are known but among organic substances this is the first example.

The creators of this class of organic ferromagnetics explain the origin of their ferromagnetism within the framework of the hypothesis of the virtual charge transfer (McConnell's second idea), although the first idea is in this instant much more reasonable.[43]

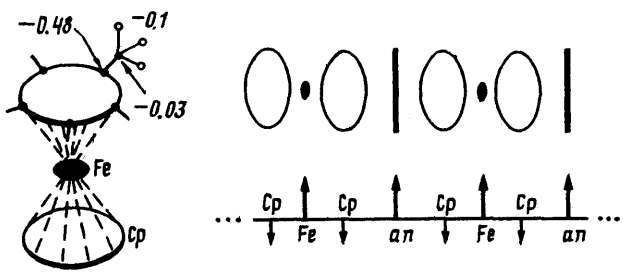
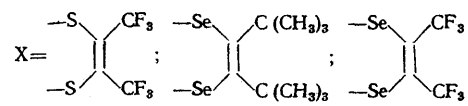


Figure 7. Schematic illustration of the spin distribution in the ferrocenium cation (on the left) and the arrangement of spins in a one-dimensional chain of a ferrocenium salt (on the right). Fe = iron atom; Cp = cyclopentadienyl ring; an = anion. The numerals denote the $^{13}C-H$ hyperfine interaction constants (in gauss).[50]

Fig. 7 illustrates schematically the arrangement of the radical-cations $[Fe(C_5Me_5)_2]^+$ and the radical-anions $(TCNQ)^-$ in a regular one-dimensional chain and, also schematically, the spin distribution in the radical-cation known from the contact paramagnetic NMR shifts for this radical-cation.[50] The π-electron spin density in the ring of the radical-cation is positive, while on the methyl groups along the perimeter of the ring the spin density is negative. McConnell islands can exist between the methyl groups of the ring of the radical-cation (negative spin density) and the CN groups of the radical-anion on which a positive spin density is localised. The McConnell islands are responsible for the alternating arrangement of the positive and negative spin densities illustrated in Fig. 7 and leading to the ferromagnetic arrangement of the spins and to ferromagnetism.

Within the framework of this concept, it is possible to explain the change in magnetic properties when the radical-anion or the metal ion is replaced in radical-ion salts of this type. Thus the salt $[Fe(C_5Me_5)_2]^+[C_4(CN)_6]^-$ is ferromagnetic, while the salt $[Fe(C_5H_5)_2]^+[C_4(CN)_6]^-$ is merely paramagnetic and shows no signs of ferromagnetic properties. It is known that the signs of the spin densities in the ligands C_5H_5 and C_5Me_5 are different and the replacement of the C_5Me_5 ligand by C_5H_5 therefore breaks up the McConnell islands, which entails the disappearance of ferromagnetism. The replacement of the $[C_4(CN)_6]^-$ paramagnetic radical-anion in the salts by the diamagnetic $[C_3(CN)_5]^-$ anion or of the paramagnetic radical-cation $[Fe(C_5Me_5)_2]^+$ by the diamagnetic cation $[Co(C_5Me_5)_2]^+$ also abolishes the McConnell islands and the substituted salts do not therefore show signs of ferromagnetism. In contrast to the ferromagnetic salt $[Fe(C_5Me_5)_2]^+[C_4(CN)_6]^-$, the salt $[Ni(C_5Me_5)_2]^+[C_4(CN)_6]^-$ is antiferromagnetic; the cause is similar because the signs of the spin densities in the C_5Me_5 ligand at the Fe and Ni ions are different (this is known from NMR[51]) and there are therefore no McConnell islands and no ferromagnetism in the nickel salt. We may note that all these substitutions should not affect the ferromagnetism if its origin were associated with the virtual charge transfer.

The first discoveries of molecular ferromagnetics among ferrocenium salts stimulated an extensive search for analogues. Thus radical-ion salts in which the anion is provided by the complex salt NiX_2, where

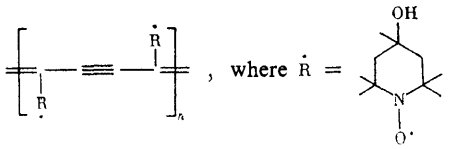


have been synthesised on the basis of $Fe(C_5Me_5)_2$. These molecules are packed in crystals in stacks with a remarkable two-dimensional architecture and the Curie–Weiss temperature is positive (about 1 K), which indicates weak signs of ferromagnetism but explicit ferromagnetics have not so far been found among these substances.[52]

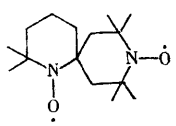
V. Organic polymers

Ovchinnikov and co-workers[53,54] achieved impressive results in the preparation of ferromagnetic organic polymers. The thermal or photochemical polymerisation of the spin-labelled diacetylene $\dot{R}-C\equiv C-C\equiv C-\dot{R}$, where $\dot{R}$ is a nitroxyl radical, yielded a polymer in which 0.1–0.3% of the overall mass consisted of particles which could be separated magnetically and whose magnetisation reached ~ 1 G g^{-1}. The Curie point is 420–460 K and sometimes higher, i.e. the ferromagnetism persists up to anomalously high temperatures adjoining the limiting temperature of the chemical stability of the polymer. The crystal structure of the

initial diacetylene[55] prevents its topochemical polymerisation, typical for the majority of diacetylenes. However, one can assume that oligomeric blocks of the type



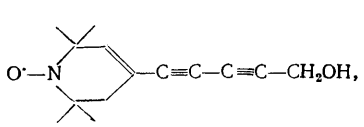
exist in the polymer. The two spin systems—one belongs to the principal polyene chain (in which the concentration of unpaired electrons is as usual high) and the other belongs to nitroxyl fragments—are independent, i.e. the exchange interaction between them is negligible. This follows from the fact that even in the initial monomer the paramagnetic fragments are independent (the EPR spectrum of the biradical consists of a triplet and is typical of a nitroxyl monoradical) and there is no exchange between the unpaired electrons through the π-system. Even in a biradical with the paramagnetic centres in close proximity, i.e.



the exchange energy is $J \ll 15$ Oe (i.e. $J \ll a$, where a represents the hyperfine electron–nuclear interaction involving the ^{14}N nucleus).[1] The low value of J is due to the barrier set up by the σ-bonds which separate the two π-electron systems.

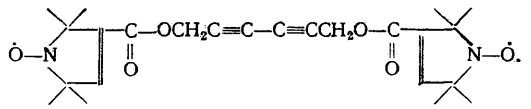
The very weak exchange interaction of the two spin systems ($J \lesssim 10^{-7}$ eV) is inconsistent with the high-temperature ferromagnetism of the polymer (there is an energy deficiency by 7–8 orders of magnitude), which means that it is not the cause of the ferromagnetism. It may be that McConnell islands are present in the structure of Ovchinnikov's ferromagnetic polymer, but it would then be necessary to assume that structures with such islands are very rigid, are not disrupted by molecular motion, and persist even at 450–500 K, where the polymer itself already undergoes chemical degradation. This is naturally a large claim for which there is no proof. At any rate, the origin of the ferromagnetism of the spin-labelled polydiacetylene remains puzzling. The structure of the polymer is just as puzzling: it is insoluble and amorphous and the type of polymerisation and the chemical mechanism of the propagation of the polymer chain are unknown; it is only known that polymerisation entails the destruction of the paramagnetic centres of the nitroxyls (sometimes to an extent up to 80%), possibly as a result of addition to multiple bonds.[56] Polymerisation can be induced by the shear deformation of the monomer under high pressure conditions (1.2 GPa, 40° and 270° shifts), which affords a dark-brown powder (resembling that formed on thermal polymerisation), but it shows no signs of ferromagnetism.[55]

The polymerisation of another spin-labelled diacetylene has been reported:[57]



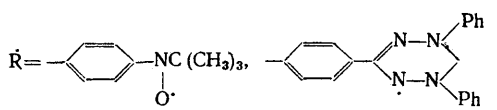
In contrast to the previous monomer, it is capable of topochemical polymerisation and its structure is much more definite. The polymer contains about 3% of a ferromagnetic fraction with a saturation magnetisation of 0.3 G cm^3 g^{-1}.[57]

Japanese workers[58] reproduced Ovchinnikov's polymer and in addition synthesised a polymer from another spin-labelled diacetylene:



Its magnetic properties are similar to those of Ovchinnikov's polymer (coercive force 300 G, saturation magnetisation ~0.2 e.m.u. g^{-1} at 30 K, residual magnetisation 2.5×10^{-2} e.m.u. g^{-1} (although the exchange interaction between the two spin systems—polyene and nitroxyl—is in this case still weaker (because the σ-bond barrier between these systems is much higher).[58]

Iwamura and Murata[6] synthesised spin-labelled polyacetylenes in another way—by the catalytic polymerisation of acetylenes CH≡ĊR, where



in the presence of the $WCl_6/SnPh_4$ catalyst. In the former case, the average number of monomer units in the macromolecule was 180, while in the latter case it was 210 and the fraction of radical spins preserved in the "living" units was 25–30%. The polymer was paramagnetic and showed no signs of ferromagnetism.[6]

In flexible-chain polymers spin-labelled with nitroxyls [styrene–maleic anhydride copolymer, poly(glycidyl methacrylate), polyfulvene, etc.], a ferromagnetic fraction (3–5%) was also found.[59] The ferromagnetic grains "follow" the magnet. After the subsequent division in two, one of the halves attains ferromagnetism, while the other loses it. The destruction of nitroxyl radicals (by thermolysis or by treatment with acids) does not destroy the ferromagnetism, i.e. there is no direct relation between paramagnetism and ferromagnetism.

The magnetisation of the flexible-chain ferromagnetic polymers is 10^{-1}–10^{-2} G g^{-1} and the Curie point is at 350–400 K. Measurements have been made of the amounts of metal ions present as an impurity (10^{-1}–10^{-2}%) and it was shown[59] that the experimentally measured magnetisations do not as a rule exceed the magnetisations calculated on the assumption that the iron ion impurities are combined into clusters consisting predominantly of α-iron. However, one cannot conclude from this that the impurity iron ions are reduced to metallic iron which is responsible for the ferromagnetism. It may be that the metal ions arrange the paramagnetic fragments of macromolecules into ferromagnetic organometallic structures (as a result of an interaction of the metal–ligand type). A similar possibility was incidentally discussed as early as 1963 by Blyumenfel'd[60] in connection with the previously discovered ferromagnetism of DNA and other biopolymers. The ferromagnetism of organic structures is naturally induced by iron impurities, but one cannot reduce it to trivial ferromagnetic contaminations (inclusions); iron ions or clusters are linked to the main organic structure in such a way that together they generate a single ferromagnetic system.[60] It is likely that these ideas will now become again of current interest.

Weak ferromagnetism is frequently observed in degraded or carbonised polymers (including cellulose) and in polymers subjected to strong shear deformation at high pressures. It has a number of unusual features (non-reproducibility, irreversible disappearance in

time, etc.) and has therefore generated much scepticism. Its origin is obscure. It can be associated with the reduction of traces of metal ions by chemical reactions induced by degradation or mechanodegradation, but one cannot exclude (although this is unlikely) the possibility of the formaton of structural clusters with McConnell islands. At any rate, the question whether or not purely organic ferromagnetic polymers without ferromagnetic metal impurities can be created remains open.

We may note a further three cases of the observation of ferromagnetism in organic polymers. The pyrolysis of polyacrylonitrile at 350 °C is accompanied by the appearance of a weak ferromagnetism (the magnetisation is 0.3–0.5 G g^{-1}), while its heat treatment at high temperatures (up to 900 °C) affords a material (pyropane) with a magnetisation of 15 G g^{-1}.[61] It consists of amorphous graphite (~80%) and an aromatic polymer (10–12%) and contains a highly crystalline phase (8–10%), which can be separated magnetically and has a magnetisation of about 150 G g^{-1} and a density of 3 g cm^{-3} (we may recall that the magnetisation of metallic iron is 200–215 G g^{-1}). The iron content in pyropane is $(1-3)\times10^{-4}$% and that in the magnetic phase is 1×10^{-2}%, which is too negligible to permit the assumption that the ferromagnetism of pyropane is due to the impurity. The idea of an intermediate graphite–diamond system in which each second carbon atom in the graphite-like lattice plane has an unpaired electron has been proposed.[61] Such an idealised structure has a theoretical magnetisation of 230 G g^{-1} and a spin concentration of about 10^{23} cm^{-3}, which is completely unusual for organic structures.[61] It has been concluded that pyropane approaches this idealised graphite–diamond structure. However, later other data indicated that the content of iron in the magnetic phase of pyropane 8% instead of 10^{-2}%,[57] but even this is too low to account for the ferromagnetism of pyropane.

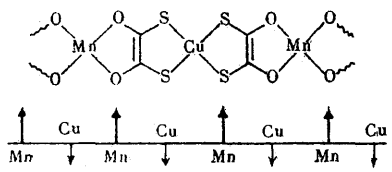
It has also been noted that, when pyropane is ground in a ball mill, its magnetisation increases with a simultaneous rise in the iron content[57] (the spheres in the ball mill were probably metallic, although this is not reported; however it is known that on treatment in a ball mill with steel or magnetite spheres, even wood filings become ferromagnetic).

Torrance[32,62] reported that the reaction of symmetrical triaminobenzene with iodine in different solvents and even in the vapour phase results in the formation of a black, insoluble polymer of unknown structure, which sometimes contains up to 2% of a ferromagnetic fraction with a magnetisation of the order of 10^{-2} G g^{-1}. It vanishes irreversibly only at ~700 K; there is also a weak hysteresis loop.[62] The results are random and non-reproducible; the polymer contains traces of iron, but, according to the author's claim,[62] its amount is smaller by a factor of 15 than that required for the "impurity" explanation of the ferromagnetism.

Finally, Japanese workers[63] have reported the appearance of ferromagnetism (0.2–0.6 G g^{-1}) in resins based on condensed polynuclear aromatic compounds. There are two remarkable features of this ferromagnetism. Firstly, it arises only on UV irradiation of the resins, i.e. on generation of radicals, and, secondly, it appears only in resins based on *meta*-substituted aromatic compounds but is absent from polymers based on *p*-xylylenes. The possibility of "native" ferromagnetism as a result of the generation of McConnell islands on photolysis have been postulated. However, a trivial explanation cannot be ruled out either: although the authors claim that there were no metals in the resins, there is a possibility that traces of metal ions were reduced to ferromagnetic chemical forms under the influence of photochemical reactions.

VI. Organometallic polymers

This class of ferromagnetics is based on multispin organometallic macromolecules in which the spins belong to paramagnetic ions. The first example of macromolecules of this type is provided by the mixed bimetallic dithiooxalate polymeric complex of manganese and copper:[64]

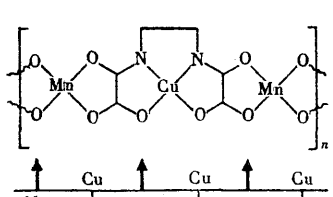


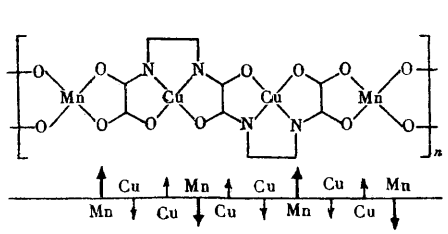
The alternating copper and manganese ions are joined together by organic ligands in such a way that each copper atom is at the centre of a planar square made up of four sulphur atoms, while each manganese atom is at the centre of a plane made up of five oxygen atoms, two pairs of which belong to two dithiooxalate ligands and the fifth is the oxygen atom of an attached water molecule.

The isolated macromolecule has a planar zig-zag shape in which the exchange interaction of the metal ions via the organic ligand is negative and arranges the spins of the ions antiferromagnetically (as shown below, underneath the chemical formula of this macromolecule). However, since the spin of the Mn^{2+} ion ($S=5/2$) is greater than that of Cu^{2+} ($S = 1/2$), the spin chain proves to be ferrimagnetic, its magnetisation increasing with decrease in temperature (when the exchange energy J_{intra} is comparable to or exceeds kT).

In the crystal, these high-spin macromolecules are arranged in parallel in stacks: an Mn^{2+} ion opposite another Mn^{2+} ion and a Cu^{2+} ion opposite another Cu^{2+} ion. The intermolecular exchange interaction arranges the spins of neighbouring ions in an antiparallel fashion, so that the overall high spin of one macromolecule is compensated by the spin of a neighbouring molecule. Therefore at T_c = 7.5 K, where $J_{inter} \simeq KT_c$, the polymer passes to the antiferromagnetic state.[64]

Kahn and co-workers[65,66] have made the greatest advances on the way to organometallic polymers. They synthesised bimetallic crystallising linear multispin macromolecules from the 1,3-propylenebisoxamate dianion:





The arrangement of spins in these macromolecules is indicated under the formulae. In both cases, the intermolecular exchange interaction between the ions is negative and arranges them

antiferromagnetically. In the first case, the macromolecule is of the high-spin type and ferrimagnetic (the overall spin of the Cu^{2+} ions does not compensate for the total spin of Mn^{2+}). However, in the crystal the intermolecular exchange interaction is negative and again the high spin of one macromolecule is compensated by the oppositely oriented spin of a neighbouring molecule, so that the crystal, made up of high-spin macromolecules, become antiferromagnetic overall at low temperatures. In the second case, the change in the sequence of ions in the chain can result in the complete compensation for the spins and the macromolecule is of the low-spin antiferromagnetic type.

The arrangement of the spins in a pair of neighbouring macromolecules with a regular alternation of Cu^{2+} and Mn^{2+} ions is illustrated in Fig. 8*a*; their compensation is evident. However, if one macromolecule is displaced relative to another by a distance equivalent to "half a ligand" (under these conditions the Cu^{2+} ions of one molecule are placed opposite the Mn^{2+} ions of another and conversely), then the arrangement of the spin changes sharply and becomes ferrimagnetic: the Mn^{2+} spins are oriented in one direction and the small Cu^{2+} spins are oriented in another (Fig. 8*b*). Such arrangement of spins had in fact been predicted previously (Fig. 5).

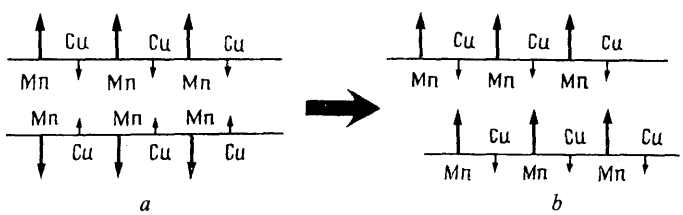
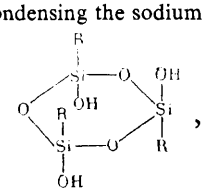


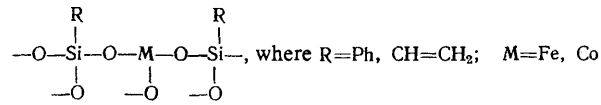
Figure 8. The transformation of the antiferromagnetic arrangement of the spins of two organometallic molecules into a ferrimagnetic arrangement by the "shift" of one macromolecule relative to the other.

The "half-ligand" shift of the macromolecule has been achieved experimentally[66] by replacing the $CH_2CH_2CH_2$ group connecting the nitrogen atoms in the ligand by the $CH_2CHOHCH_2$ group. The resulting organometallic polymer did indeed prove to be a low-temperature ferromagnetic with typical properties, including a hysteresis group.[66] The same workers obtained a similar ferromagnetic on the basis of another ligand—the oxamidobisbenzoate dianion.[67]

In essence, all these polymers are polymeric complexes of organic ions with organic ligands which were synthesised by methods of inorganic chemistry. Procedures are also being developed to produce ferromagnetics based on organometallic polymers with paramagnetic metal atoms bound covalently in the main polymer chain. A notable example is provided by polymetallosiloxanes,[68] which were obtained by condensing the sodium salt of cyclotrisiloxane, i.e.


, where R = Ph, CH=CH$_2$,

with metal salts ($FeCl_3$, $CoCl_2$, etc.) in anhydrous solvents. They contain the fragments


, where R=Ph, CH=CH$_2$; M=Fe, Co

with alternating—SiOM—and—SiOSi—bridges, as well as siloxane rings, open chains, and cross-linked structures. Polymer fractions with an M : Si ratio ranging from $10^{-3}-10^{-2}$ to 1.5 can be isolated by fractional precipitation. In the fractions with a high M : Si ratio, the—$MO(SiOSiO)_nM$—molecular fragments with high values of n are replaced by short fragments with $n = 1$ and even $n = 0$ (—MOM—).

In order to convert such paramagnetic polymers into ferromagnetics, it is necessary to achieve an exchange interaction between the metal atoms. There are various ways of doing this: by shortening the bridges between the atoms, making them "conducting" to the exchange interaction; by creating new additional bridges; and finally by removing the organic bridges altogether and joining together the paramagnetic atoms.[68] All these versions are being actively developed. The simplest is attained in the high-temperature pyrolysis of ferropolysiloxane. A considerable proportion of the organic component of the molecule is then removed and a ferromagnetic composite material with a magnetisation of 10—50 G g^{-1} is produced (depending on the metal content and the pyrolysis temperature). It contains iron silicide and carbide phases, amorphous silicon dioxide, and carbon, as well as 300—350 Å α-ion clusters.[68] As regards their dynamic properties, these high-temperature ferromagnetics belong to the rigid class: in the wavelength range 0.8—30 cm, their magnetic permeability is close to unity and the tangent of the magnetic loss angle is negligible. This aspect of the chemical construction of ferromagnetics is closely related to the modern materials science of metal-filled polymeric composites.

VII. Conclusion

The principal achievements of the science of organic ferromagnetics are the recognition and understanding of the physical principles of their construction and the chemical pathways leading to it; there exists reliable theoretical and experimental evidence showing that these procedures are realistic; finally, the first "genuine" organic ferromagnetics exist.

Problems and difficulties can be clearly seen; the main one is the problem of the molecular organisation of multispin and high-spin molecules in a "solid state" order such that a ferromagnetic arrangement of the spins is ensured. This problem is soluble (we have seen brilliant examples of such solutions), but requires serious intellectual efforts.

One must clearly recognise also the deficiencies of organic ferromagnetics as potential magnetic materials. They all arise from the fact that organic molecules contain a lot of "dead weight"—a ballast consisting of spinless groups and fragments which results in a low spin density, i.e. a small number of spins per unit volume of the substance. Thus metallic iron contains 4×10^{23} spins per cm^3 while their number in an organic ferromagnetic is smaller by 1—2 orders of magnitude. This gives rise, firstly, to low magnetisations (smaller by 1—3 orders of magnitude than in iron) and, secondly, to low exchange energies (because of the large interspin distances), resulting

in low temperatures of transition to the ferromagnetic state (in other words, "genuine" organic ferromagnetics should be as a rule low-temperature materials); thirdly, the dipole interaction of the spins is also weak and this hinders the formation of a domain structure and spontaneous magnetisation. Finally, one should bear in mind the chemical instability of organic materials, the "ageing" of magnetic materials based on them as a function of time, and the restricted operational usefulness of such materials under severe thermal conditions or in oxidising media. Organic ferromagnetics are hardly likely to have superior static magnetic properties compared with classical metallic ferromagnetics but they can possess unusual dynamic properties—magnetic and dielectric losses and their frequency dependence.

From technical standpoints, the polymeric organic ferromagnetics are naturally the most attractive, although there is no certainty that such polymers can exist in the absence of impurities or traces of metals.

The problem of ferromagnetic impurities and inclusions (especially for low magnetisations) is most acute for polymers. The problem is tricky for the following reasons. On the one hand, impurities are discouraging, creating the impression of a "non-genuine" ferromagnetic, and destroy the stimulus to scientific research. On the other hand, if impurities are incorporated in an organic structure and organise its paramagnetic component (spin labels, polyconjugated systems, etc.) into a ferromagnetic order, we have a success, an achievement. It is then necessary to learn how to control this process—how to introduce such impurities into such polymers and in a way ensuring the maximum "synergism" of the organic and inorganic components in the generation of ferromagnetic organo-metallic structures. Here there is only one procedure—quantitative comparison of impurities with magnetisation. The problem is not yet clear: in some cases the impurities are sufficient to ensure the observed ferromagnetism, whilst in others their content is insufficient by 1–2 orders of magnitude. However, the unreliability of the analyses for metallic impurities and the non-reproducibility of the results leave open this part of the problem of organic ferromagnetics (although it is entirely clear how it could be "closed").

At the present level of knowledge, mixed organometallic ferromagnetics merit most attention, although overall the entire field of organic ferromagnetics merits vigorous development. Nor can one ignore its useful forays into adjoining fields, in particular into the chemistry of multispin and high-spin molecules as the potential elementary basis of the future molecular electronics.

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The conformational analysis of organoelemental and organometallic molecules

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ABSTRACT. The results obtained using the mechanical model of a molecule to calculate the conformation and conformational transformations of the molecules of organoelemental and organometallic compounds have been reviewed. The conformational characteristics of the molecules of hydrocarbons and their organoelemental analogues have been compared. The present state and future prospects of the use of the mechanical model in calculations for the molecules of π-complexes and metal clusters have been described.

The bibliography contains 134 references.

Contents

I. Introduction 320
II. The mechanical model of a molecule 320
III. Conformational calculations for organoelemental molecules 321
IV. Conformational calculations for organometallic molecules 333
V. Summary 341

I. Introduction

Conformational analysis in the wider sense involves the study of the relative arrangement of the parts of a molecule and the possibility of a change in this arrangement, taking place without the rupture of chemical bonds, and also the search for the relationship between the reactivity of molecules and their conformation. This analysis includes an examination of both the geometric (bond lengths, valence and torsional angles, non-valence contacts) and the energetic (the relative energies of the conformers and isomers, the barriers to internal rotation, etc.) characteristics of the molecules. The conformers are studied by experimental methods and calculations, and the accessibility of the latter has increased considerably with the significant development of computer technology.

The principal experimental methods for studying the conformation of molecules at present are X-ray diffraction (XRD), neutron diffraction (for molecules in the crystalline state), NMR (for molecules in the liquid state), gas-phase electron diffraction (GED), and spectral methods (for molecules in the gaseous state). All these methods have their advantages and limitations, the most significant limitation being that the results of a study of the structure of molecules in one phase state (particularly for the conformation of non-rigid molecules) cannot be transferred to another phase state without additional analysis (most frequently by calculation).

The calculation methods for studying the conformation of molecules now include semi-empirical and non-empirical quantum-chemical methods, and also empirical methods which use the mechanical model of a molecule (MMM)†, based on the atom–atom approximation.

The possibility of examining a wide range of materials and the considerable saving of machine time (compared with quantum-chemical methods) has now enabled the MMM to occupy an important place among methods used to study molecular conformations. The MMM began to be used for simple organic molecules about 40 years ago,[1,2] and is now used extremely widely in organic and bio-organic chemistry.[3–6] The MMM has also been used for a fairly long time in coordination chemistry.[7,8] In these fields, the method, which has passed through a period of methodological construction and development, is used to solve specific chemical problems. The present paper reviews for the first time the available data on new fields of application of the MMM in the study of the conformational characteristics of organoelemental and organometallic molecules (in particular π-complexes), which have developed significantly only in recent years.

II. The mechanical model of a molecule

The mechanical model of a molecule is an empirical approximation based on the Born–Oppenheimer principle, which makes it possible to examine the motion of nuclei and electrons separately. In this model, the molecule is regarded as a system of interacting atoms, and the intramolecular and non-valence interactions are central in character. For each type of atom there are "ideal" values of the valence angles and bond lengths, deviations from which require the expenditure of energy. To reproduce the experimental values of the dihedral angles and the barriers to rotation about the bonds in the molecules, the model is usually supplemented by a so-called torsional component characterising the expenditure of energy due to the deviation from the optimum relative orientation of the fragments of the molecules joined by chemical bonds. Where necessary, the model also takes account of the energy of electrostatic interactions, hydrogen bonds, etc.

Thus the conformational energy of a molecule (representing the fraction of its total energy which depends on the conformation) can be written as

$$U_{conf} = U_{non\text{-}v} + U_{bd} + U_{ang} + U_{tors} + U_{el} + \ldots$$

† A number of equivalent names are used in the Soviet and other literature for calculations of this type, for example "molecular mechanics", "force-field calculations", etc.

Here, the energy of the non-valence interaction ($U_{non\text{-}v}$) is the sum of the paired interactions of all the atoms (atom–atom approximation), and is most frequently described by the Lennard–Jones ("6–12") or Buckingham ("6-exp") potentials:

$$U_{non\text{-}v} = -Cr^{-6} + Ar^{-12},$$
$$U_{non\text{-}v} = -Cr^{-6} + A\exp(-Br),$$

where r represents the interatomic distances, and A, B, and C are empirical constants, obtained, for example, from the virial coefficients and the equilibrium interatomic distances for the inert gases.

The terms U_{bd} and U_{ang} are the energies required to deform all the bonds and valence angles in the molecule from the ideal values (l_0 and θ_0), for which the mean-statistical values are often taken‡, to the actual values (l and θ). For the small deformations usually observed with change in the conformation, Hooke's law (the harmonic approximation) is applicable:

$$U_{bd} = 0.5K_l(l-l_0)^2,$$
$$U_{ang} = 0.5K_\theta(\theta-\theta_0)^2,$$

where K_l and K_θ are the force constants of the bonds and angles, obtained from the vibrational spectra of the simple molecules. The torsional energy (U_{tors}) is written as

$$U_{tors} = 0.5U_0(1+\cos n\varphi),$$

where U_0 is the torsional constant (inherent barrier), selected from experimental or quantum-chemical data on the barriers to internal rotation, φ the dihedral (torsional) angle for the kth bond, and n the multiplicity of the barrier to rotation.

The energy of the electrostatic interactions (U_{el}) is taken into account fairly infrequently, sometimes in the dipole–dipole or, more often, in the monopole approximation:

$$U_{el} = q_i q_j/\varepsilon r_{ij},$$

where q_i and q_j are the charges on the ith and jth atoms (obtained from a quantum-chemical calculation) situated at a distance r_{ij} from one another, and ε the dielectric constant (usually, $\varepsilon = 1$).

The geometry of an isolated (free) molecule corresponds to a conformational energy minimum. Thus the determination of the optimum molecular conformation involves the search for a minimum value of U_{conf}.

Depending on the form of representation of the coordinates of the atoms in the molecule (Cartesian or coordinates expressed in terms of the bond lengths and valence and torsional angles—the so-called "tree system"), different methods of minimising U_{conf} are used, and these have been described in detail.[3,4] In the general case, the problem of determining the optimum geometry of a molecule reduces to the search for a minimum of a function of $(3N-6)$ variables, where N is the number of atoms in the molecule. Fairly frequently, however, most of the geometric parameters of the molecule can be fixed, so that the problem is simplified, and reduces to scanning the values of U_{conf} over several variables (constructing the corresponding graphs and conformational maps). The search for the minimum of U_{conf} over all variables is naturally possible only for molecules in which the number of atoms is not too large, up to ~100, whereas when the number of parameters is restricted, it is possible to examine the conformation of very large molecules, for example proteins. The molecule is usually described in the Cartesian system of coordinates in the first case, and using the "tree system" in the second. Both of these methods of specifying the geometry and the corresponding methods for finding the minimum of U_{conf} have been used in a large number of computer programs. The first of these methods is employed, for example, in the widely used programs MM2 and MMP2 of Allinger and co-workers[4] and in Boyd's program MOLBD3,[9] and the second is used in the program ECEPP of Scheraga and co-workers[10] for calculating peptide structures.

The choice of parameters for conformational calculations will not be dealt with in detail. The most widely encountered method of finding the parameters—the constants in the expressions for the components of U_{conf}—is by variation for a series of simple compounds of the same type to achieve the best agreement between the calculated and experimental data (the geometric parameters of the molecules, the barriers to internal rotation, etc.) or corresponding data obtained in a non-empirical quantum-chemical calculation. Data on the specific sets of parameters proposed by different authors for groups of compounds of the same type will be given in the appropriate sections.

III. Conformational calculations for organoelemental molecules

The similarity in the structures of hydrocarbons and organoelemental compounds in which one or several C atoms have been replaced by the atoms of an element X = Si, Ge, Sn, Pb is fairly obvious (the tetrahedral coordination of the atoms C and X, the formation of ordinary σ-bonds, the absence of lone pairs of electrons). Conformationally, however, the molecules of hydrocarbons and their organoelemental analogues (linear and cyclic) may differ considerably. This led to the idea of using the MMM to calculate the conformations of these molecules to investigate the reasons for their similarities and differences.[11–13] Two large groups of compound forming acyclic and cyclic molecules will be considered as an example of how this problem was solved.

1. Acyclic organoelemental molecules

Parameters of the potentials have been proposed[11–13] for the calculations for organoelemental molecules (X = Si, Ge, Sn), and a number of calculations have been carried out for fairly simple molecules, to verify the suitability of the proposed parameters. Most of the calculations have been carried out for organosilicon molecules,[11,12] since they have been more fully characterised by physicochemical methods. The good agreement between the calculated and experimental data made it possible to use the proposed parameters with confidence for carrying out specific calculations.

The relative energetic advantage of the conformers and the barriers to conformational transformations have been examined[13] for various simple hydrocarbons and their organoelemental analogues in which one of the C atoms has been replaced by an X atom. In the compounds $MeHX_3$, Me_2XH_2, and Me_3XH, on going from X = Si to X = Ge and Sn, the barrier to rotation about the C–X bond decreases considerably, the values being 1.6 (X = Si), 1.2 (X = Ge), and 0.65 (X = Sn) kcal mol^{-1} respectively. This is attributed to the decrease in the contribution of the non-valence interactions to the magnitude of the barrier, as a result of the increase in the length

‡The mean-statistical values of the geometric parameters are calculated for the isolated molecules in the gas phase from GED data or for the molecules in the crystal from XRD data, collected in the Cambridge Structural Data Bank.

of the C–X bond, and to the simultaneous decrease in the torsional constant for this bond, which has the values 0.5, 0.38, and 0.22 kcal mol^{-1} for X = Si, Ge, and Sn respectively.

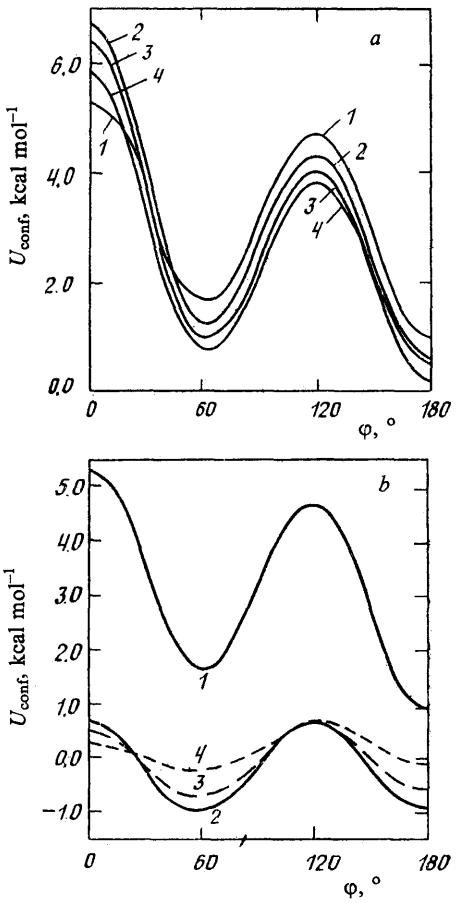


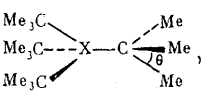
Figure 1. Dependence of U_{conf} on the angle of rotation about the central bond in the molecules $CH_3CH_2CH_2XH_3$ (*a*) and $CH_3CH_2XH_2CH_3$ (*b*), where X = C (*1*), Si (*2*), Ge (*3*), and Sn (*4*).[10]

The introduction of an organoelemental substituent on one of the C atoms has little influence on the magnitude of the barrier to rotation about the C–C bond. Thus for the molecules $CH_3CH_2XH_3$, these barriers have the values 3.78, 3.87, and 3.98 kcal mol^{-1} for X = Si, Ge, and Sn respectively.

A calculation made it possible to estimate[10] the ratio of the relative energies of the *gauche* (or crossed, φ = 60°) and *anti* (or *trans*, φ = 180°) conformations (rotation about the central bonds) for the molecules $MeCH_2CH_2XH_3$ and $MeCH_2XH_2Me$. In the first case (Fig. 1*a*), the introduction of the atom X into the terminal group does not change the conformation of the molecule relative to n-butane, and only leads to a slightly greater difference in the energies of the eclipsed and staggered conformations. This is understandable, since in this case the central bond does not change, and the terminal groups are "repelled" more strongly in the eclipsed conformation, since they are brought closer together by the increase in the length of the C–X and X–H bonds. In the second case, the *trans*- and *gauche*-conformers of $MeCH_2XH_2Me$ (unlike the corresponding conformers of n-butane) have similar energies (Fig. 1*b*). The explanation is that the increase in the length of the central bond in the molecule is associated with an increase in the contribution made to U_{conf} by the energy of attraction between the H atoms of the terminal methyl groups, favouring the approach of these groups, that is the energy of the *gauche*-conformation approaches that of the *trans*-conformation.

Mislow and co-workers[14–19] examined not only the relative advantage of the conformers and the values of the barriers to rotation but also the mechanism of internal rotation in molecules, in particular the mechanism of the rotation of several bulky substituents situated on one C or X central atom. Thus the rotation of the t-butyl groups in the $HSi(Bu\text{-}t)_3$ molecule was analysed.[19] Here, two mechanisms of internal rotation of the alkyl substituents are possible: independent and coupled, that is involving the simultaneous rotation of at least one other substituent. In the case being considered, only coupled rotation takes place. The rotation of the t-butyl groups can take place in two ways: all three t-butyl groups may be present simultaneously in the staggered (*S*) orientation (*SSS*, barrier to rotation 5.1 kcal mol^{-1}), or one of the groups may be present in the eclipsed (*E*) orientation, and the other two in the staggered orientation (*ESS*, barrier 6.8 kcal mol^{-1}). The fact that the magnitude of the second barrier is close to the experimental value obtained from NMR data, $\Delta G^{\neq}$ = 6.1 ± 0.3 kcal mol^{-1}, was taken as evidence that the actual mechanism of internal rotation is of the *ESS* type.

For two series of sterically crowded molecules $X[CMe_3]_4$ and $X[SiMe_3]_4$, where X = C, Si, Ge, Sn, and Pb, calculations have been carried out[18] to determine the geometric parameters of the molecules (there are no published experimental data for molecules of the first type) and to compare the energies of their conformers with *T* and S_4 symmetry. The results of the calculation for the molecules



where X = C, Si, Ge, Sn, Pb, are summarised in Fig. 2. Fig. 2 shows that the difference in the values of U_{conf} for the energetically more favourable (*T*) and less favourable (S_4) conformers (ΔU_{conf}) decreases with increase in the atomic number of the central atom. At the same time, the angle θ increases, and its value approaches the usual tetrahedral value. For the first member of the series (X = C), for which the steric crowding is greatest, the decrease in this angle is fairly large. The same trend in the change in the geometric and energetic parameters was detected in the series of molecules $X[SiMe_3]_4$.

A search for the most favourable conformations and an analysis of the routes of conformational rearrangements has also been carried out for aryl-substituted§ derivatives of methane and silane.[15,16] The most favourable conformations were found to be that with D_{2d} symmetry for the CPh_4 molecule, and that with S_4 symmetry for the $SiPh_4$ molecule.[15] It was pointed out[15] that this result was not obtained for these compounds in earlier calculations,[20] since the authors of these calculations did not vary all the geometric parameters, but only the values of the torsional angles round the C–Ph or Si–Ph bonds. For the molecules CR_4 and SiR_4, where R = *o*-tolyl or 2,6-xylyl, the S_4 conformers were found to be most

§The parameters of the potentials for conformational calculations for molecules containing an Si–Ar bond have been published.[15]

favourable.[15] A calculation to analyse the mechanism of internal rotation in molecules of this type showed[15] that the rotation of the substituents in this case, as in the case of the t-butyl derivative of silane, is not independent, and the route of the conformational transformation can be represented by the sequence of conformers shown in Fig. 3. Although the molecules with the *o*-tolyl substituents are less symmetrical, and a large number of conformational transformation routes are possible for these molecules, the most favourable mechanism of rotation for these molecules was found to be similar to that found for the Ph-derivatives. The calculated values of the barriers to the internal rotation of the substituents for the molecules of $SiPh_4$ and $Si(o\text{-}CH_3C_6H_4)_4$, 14.9 kcal mol^{-1} and 19.6 kcal mol^{-1} respectively, lie in the range of values of the activation energy of the topo-isomerisation process obtained experimentally from NMR data.

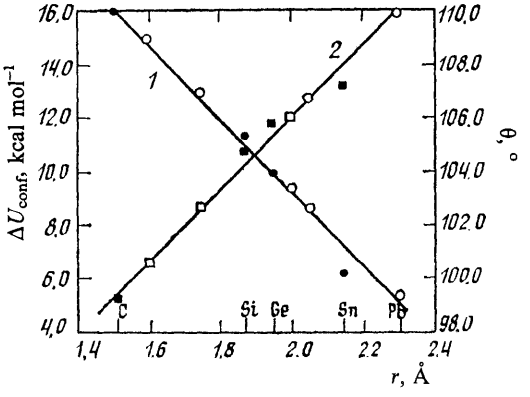


Figure 2. Dependences of the difference in the energies ΔU_{conf} (*1*) between the *T*- and S_4-conformers and of the angle θ (*2*) on the C–X bond length in $X(CMe_3)_4$ molecules, where X = C, Si, Ge, Sn, Pb;[18] the black points correspond to the actual structures, and the white points to model structures with intermediate values of the C–X bond lengths.

Stereo-isomerisation has been examined[14] for a large number of triaryl-substituted molecules. The authors cited used a simplified approach, in which the same parameters [as for the $HC(Mes)_3$ molecule] were used for the molecules $Z(Mes)_3$, where Z = B, CH, SiH, GeH, N, P, and As, and Mes = mesityl, and only the length of the Z–Mes bond was changed. The calculation of the routes for the simultaneous internal rotation of one, two, and three substituents (Fig. 4) showed that the simultaneous rotation of two aryl fragments is most favourable in this case. The calculated and experimental values of the barriers to rotation in these molecules are compared in Fig. 5. The calculation provides a qualitatively correct description of the change in the magnitude of the barrier with change in the Z–Mes bond length, but it does not reproduce the experimental values quantitatively. This last feature (the high values of the barriers) was attributed to the use of a simplified model, in which the lengths of the bonds formed by the central atom Z in the molecule were not varied.

Halogen-substituted alkylsilanes of the type $Si(CH_2Hal)_4$, $H_2Si(CHal_3)_2$, and $Hal_2Si(CHal_3)_2$, where Hal = F, Cl, Br, have been studied.[21,22] For the tetra-substituted molecules,[21] for all Hal, the conformation with D_{2d} symmetry is most favourable. The order of the relative advantage of the conformers is different for different halogens, however: $D_{2d} > C_s > C_2 > C_1 > S_4$ for F, $D_{2d} > C_4 > C_1$ for Cl, and $D_{2d} > S_4$ for Br. The conformation with C_2 symmetry is most favourable for the dialkyl-substituted molecules $H_2Si(CHal_3)_2$, and that with C_{2v} symmetry is most favourable for $Hal_2Si(CHal_3)_2$. The calculated barriers to the internal rotation of the substituents are 5.7, 14.5, and 14.8 kcal mol^{-1} for F, Cl, and Br respectively in the molecules $H_2Si(CHal_3)_2$, and 2.2, 8.2, and 8.5 kcal mol^{-1} respectively for $Hal_2Si(CHal_3)_2$.

Parameters making it possible to use the mechanical model of a molecule to carry out calculations for allylsilanes have been proposed.[23] The parameters were selected by fitting the results of calculations using the MMM to the results of non-empirical quantum-chemical calculations using different basis sets. The torsional potential of the rotation about the central bond in the fragment C=C–C–Si was found to be close to the usual value for rotation about a $C(sp^2)$–$C(sp^3)$ bond. The minimum energy

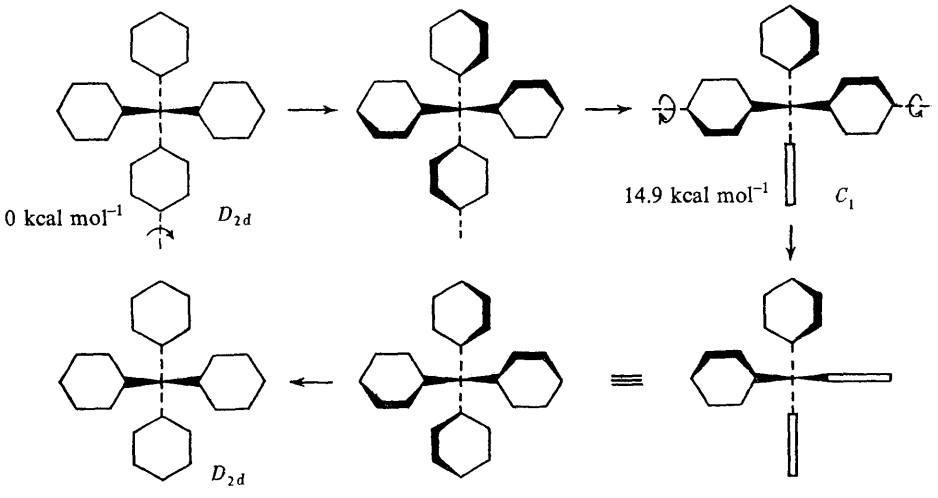


Figure 3. Internal rotation pathway in tetraphenylmethane.[15]

corresponds to the conformation of allylsilane with a torsional angle of rotation round the central bond equal to ~100°; the values of the *cis*- and *trans*-barriers differ slightly, and according to the data obtained using the MMM (in agreement with quantum-chemical calculations) are equal to 2.09 kcal mol^{-1} and 2.75 kcal mol^{-1} respectively.

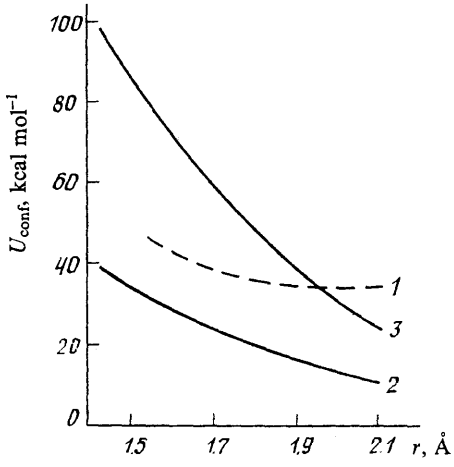


Figure 4. Calculated energies of the transition state for different mechanisms of the stereo-isomerisation of $Z(Mes)_3$ molecules: *1*, rotation of one mesityl substituent; *2*, two substituents; and *3*, three substituents (r is the $Z-C_{Mes}$ bond length).[14]

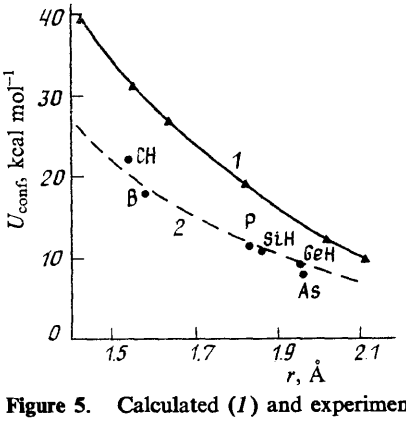
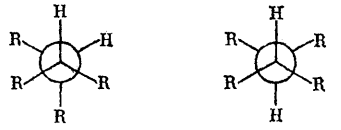


Figure 5. Calculated (*1*) and experimental (*2*) values of the energy of stereo-isomerisation for $Z(Mes)_3$ molecules (r is the length of the $Z-C_{Mes}$ bond).[14]

A parametrisation which makes it possible to carry out conformational calculations for molecules containing chains of several Si atoms was described by Mislow and co-workers[24] and developed in later studies.[25] The simplest representatives of this series are the alkyl-substituted disilanes $(R_2HSi)_2$, where R = Me, t-Bu, and Cy (cyclohexyl).[26] For the compound with R = Me, the energies of the *gauche*- and *anti*-conformations



according to the calculations, differ by 0.2 kcal mol^{-1}, but the barriers to the transformations $G \rightleftarrows G^-$ and $G \rightleftarrows A$ are fairly small: 0.97 kcal mol^{-1} and 1.34 kcal mol^{-1} respectively. The dependence of U_{conf} on the angle of rotation about the Si–Si bond in the $[(t\text{-Bu})_2HSi]_2$ molecule is shown in Fig. 6. In this case the barriers to the corresponding conformational transformations are significantly larger: 24.9 kcal mol^{-1} for $G \rightleftarrows G^-$ and 15.1 kcal mol^{-1} for $G \rightleftarrows A \rightleftarrows A^- \rightleftarrows G^-$; the last value is close to the experimental value obtained by NMR ($\Delta G^{\neq}$ = 13.8 ± 0.3 kcal mol^{-1}). For $(Cy_2HSi)_2$, for which the number of possible conformers is appreciably greater than in the previous cases (45 *gauche*- and 27 *anti*-forms), the most favourable conformer was again found to be one of the *gauche*-conformers, whose structure shows good agreement with that found in the crystal by XRD.

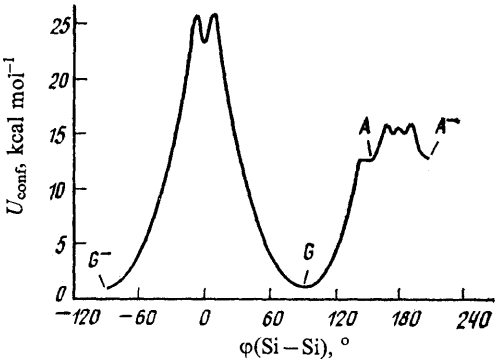


Figure 6. Dependence of U_{conf} on the angle of rotation about the Si–Si bond in the $[(t\text{-Bu})_2HSi]_2$ molecule.[26]

The stereochemistry of similar tetra-aryl-substituted disilanes has been studied[27] using the MMM, XRD, and NMR. For the $(Ph_2HSi)_2$ molecule, the energies of five *G*- and *A*-conformers are similar (the energies of the most favourable C_2– and C_i-conformers are –7.12 kcal mol^{-1} and –6.68 kcal mol^{-1} respectively). For the $(Mes_2HSi)_2$ molecules (in contrast to the alkyl derivatives described above), the *anti*-conformation becomes much more favourable [$U_{conf}(A)$ = 10.55 kcal mol^{-1}, $U_{conf}(G)$ = 13.08 kcal mol^{-1}]. The results of the calculation for the two molecules show good agreement with NMR data (in solution, the Ph-derivative exists as a mixture of conformers, whereas for the Mes-derivative the *anti*-form with C_2 symmetry predominates) and with XRD data for these compounds, according to which both derivatives are present in the crystals as the *anti*-conformers.

Molecules containing chains of several Si atoms have been examined.[24,25] The study of these molecules is a necessary stage in the determination of the structure of polymeric silane molecules. The parametrisation used in the works cited, and hence the results of the calculations, differ slightly. Table 1 compares the results of the calculations with the available experimental data for the molecules studied. The results obtained with the parametrisation proposed by Hönig and Hassler[25] show better agreement with the experimental data (Table 1). This last feature apparently explains why this version of the parameters was used to calculate the conformation of the polymer chains of polysilane $H(H_2Si)_nH$ and polydimethylsilane $Me(Me_2Si)_nMe$.[29] In the work cited, a calculation of the conformations of polysilane molecules containing n = 30, 10, and 5 units was used to analyse the dependence of the qualitative results obtained on the length of the chain being studied. The minimum chain length making it possible to model all its possible conformations was found to be that with n = 5. The data obtained for the chain with n = 5 can be used to obtain a sufficiently full description of the conformtion of longer chains. This made it possible, in the study of the conformation of polydimethylsilane, to consider only a fragment of the chain with n = 5. These calculations were repeated by Welsh and co-workers[30] with slight restrictions, in that account was taken of only the non-valence and torsional components of the energy, and also by Tashiro and co-workers,[31] where the parametrisation for the silanes (for the program MM2) was calibrated from the results of quantum-chemical calculations for model molecules.

Table 1. Comparison of the results of conformational calculations and experimental data for silane molecules.

Molecule	Confirmation	U^{rel}_{conf}, kcal mol^{-1}		ΔU, kcal mol^{-1} (method)
		Hummel et al. (Ref.24)	Hönig and Hassler (Ref.25)	
Disilane**	*S*	0.0	0.0	1.22 (IR)
	E	1.20	1.20	
Hexamethyldisilane	*S*	0.0	0.0	—
	E	1.05	1.20	
Tetrasilane	*A*	0.10	0.31	0.0 (ESCA)
	G	0.0	0.0	
Decamethyltetrasilane	*A*	0.0	0.0	0.55 (NMR, IR)
	G	0.12	0.55	

*See the paper by Hönig and Hassler[25] for references to experimental work.

**According to a non-empirical quantum-chemical calculation,[28] the relative energies of the *S*- and *E*-conformers are 0.0 and 3.8 kcal mol^{-1} respectively.

The results of the calculations for a chain with n = 5, carried out by Damewood and West[29] and Welsh and co-workers[30] (Table 2), and also by Tashiro and co-workers,[31] agree well with one another, and indicate that the *GG*-conformer is the most favourable. The differences, given below, in the conformational energies of the *anti*- (planar zigzag) and *gauche*- (spiral) conformers for alkane and silane chains[31] indicate an increase in the energetic advantage of the *gauche*-conformer for the silane and of the anti-conformer for the alkane with increase in the chain length:

n	4	5	7	13	17	21	30
ΔU (C_nH_{2n+2}), kcal mol^{-1}	0.86	1.62	2.99	7.09	10.01	12.88	19.05
ΔU (Si_nH_{2n+2}), kcal mol^{-1}	0.07	0.02	−0.16	−0.53	−0.83	−1.12	−1.82

Table 2. Relative energies of different conformers of polysilane and polydimethylsilane, kcal mol^{-1}.

Conformer	Polysilane		Polydimethylsilane	
	Profeta et al. (Ref.23)	Stolevik and Bakken (Ref.22)	Profeta et al. (Ref.23)	Stolevik and Bakken (Ref.22)
AA	0.51	0.7	0.42	0.9
AG	0.21	0.4	0.00	0.8
GG	0.00	0.0	0.08	0.0
G^+G^-	0.41	0.4	—*	38.4

*Large quantity, not calculated.

A statistical analysis of the conformational stability of polysilane chains has been carried out.[30] The calculation showed that the characteristic ratio

$$C_\infty = \lim_{n\to\infty} \langle r^2\rangle_0/nL^2,$$

where $<r^2>_0$ is the mean-square distance between the ends of the chain, n the number of units, and L the length of the unit in the chain, is 4.02 for polysilane, and 12.2−15.0 for polydimethylsilane (depending on the method used to calculate the conformational energy). Comparison of these values with the values of C_∞ for polyethylene (6.7) and polydimethylsiloxane (6.4) indicates that the polydimethylsilane molecule is less flexible than these polymers.

The influence of lateral substituents on the conformation of a polysilane chain has not been studied by calculation, but it can be followed from experimental studies of the structure of polymers of the type $R-(SiR_2)_n-R$. The polymer with R = n-pentyl has a spiral chain conformation (7/3 spiral), and that with R = n-hexyl has a planar zigzag conformation, which is apparently stabilised by the regular packing of the lateral substituents.[32,33] In the opinion of the authors cited,[32] the existence of extended chain fragments with the *trans*-conformation is responsible for the unusual spectral properties of the hexyl-derivative (the displacement of the absorption band to the low-wavenumber range 370−380 nm), not observed for its homologues with n < 6.

The fluorescence of the n-hexyl-derivative in the near ultraviolet range (λ_{max} = 300−400 nm) has also been attributed to the presence of planar *trans*-fragments.[34] Experimental data and quantum-chemical calculations indicate that the chain in this macromolecule effectively breaks down into a number of planar chromophores separated by sections with the *gauche*-conformation, between which rapid exchange of energy takes place.[34]

No experimental data have yet been published on the stucture of diphenyl-substituted polysilanes $R-(SiPh_2)_n-R$, but their conformation can be characterised from XRD data for the oligomers with

chain length $n = 4-7$.[35,36] The conformation of the phenyl-substituted polysilanes changes from planar to spiral with increase in the length of the oligomer chain. This last feature (and the fact that, as shown above, the chain with $n = 5$ repeats the conformation of the corresponding polymer) indicates that the corresponding polymers also contain chain fragments with the spiral conformation.

2. Organoelemental molecules containing cyclic fragments

A number of authors[12,37-41] have examined the influence of organoelemental substituents on the conformation of saturated cyclic hydrocarbons, and also the relative advantage of different arrangements of the substituents in them, in particular the equatorial (*e*) and axial (*a*) arrangements. Calculation has shown[12] that in mono-substituted cyclohexanes containing organoelemental substituents, as in those containing organic substituents, the equatorial arrangement is most favourable; its energetic preference compared with the axial arrangement (ΔE) for different substituents is given below:

R	Me	SiH_3	Me_2CH	Me_2SiH	Me_3C	Me_3Si
ΔE, kcal mol^{-1}	1.77	1.26	2.05	1.94	5.41	3.41

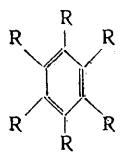
In this case, equatorial substituents have practically no influence on the conformation of the ring, whereas axial substituents lead to slight flattening.

In 1,2-disubstituted cyclohexanes[37] with comparatively small substituents (Me, SiH_3), the di-equatorial *trans*-arrangement is most favourable, as indicated both by calculations using the MMM and by non-empirical quantum-chemical (QC) calculations[37] (Table 3). For bulky substituents, the di-axial conformation is more favourable (Table 3). For $SiMe_3$ this is the only favourable conformation, but for CMe_3 the twist conformation has a similar energy. The results of the calculation show good agreement with NMR data,[36] which show that the solution of the first compound contains one conformer, whereas the solution of the second contains a mixture of two conformers.

Table 3. Relative energies of 1,2-disubstituted cyclohexanes (kcal mol^{-1}) from MMM data and QC calculation.

Conformation	Me		SiH_3		CMe_3	$SiMe_3$
	MMM	QC	MMM	QC	MMM	MMM
e,a-cis	1.62	1.96	0.78	1.16	5.29	1.80
a,a-trans	2.44	2.76	0.70	1.69	0.0	0.0
e,e-trans	0.0	0.0	0 0	0.0	6.73	1.70
twist-trans	5.40	8.15	5.80	6.50	0.41	2.34

The influence of bulky substituents, including group IV elements, on the conformation of the aromatic ring in hexa-substituted benzenes, and also the possibility and the mechanism of the internal rotation of these substituents, have been studied by Mislow and co-workers.[38-41] The problem was solved by a combination of experimental methods (NMR, XRD) and calculations. The following series of compounds was studied:



(I)—(VI)

(I): R = CH_2Me (Ref.38),
(II): R = $CHMe_2$ (Ref.39),
(III): R = $SiHMe_2$ (Ref.40),
(IV): R = CMe_3 (Ref.41),
(V): R = $SiMe_3$ (Ref.41),
(VI): R = $GeMe_3$ (Ref.41).

According to the calculations, which show good qualitative agreement with XRD data, the ethyl, isopropyl, and dimethylsilyl substituents do not distort the planar structure of the aromatic ring. These distortions are detected, however, when the bulkier trimethylgermyl substituent is introduced. The C—C bond length in the benzene ring is increased considerably (to 1.418 Å) relative to the value 1.384 Å in non-substituted benzene, the ring acquires a flattened chair conformation, and the arrangement of the $GeMe_3$ substituents, which are displaced considerably from the average plane of the central ring, is described as a "superchair" conformation. The average value of the torsional angles Ge—C—C—Ge is 57.1° (XRD), in good agreement with the results of the calculation. The same trend in the distortion of the benzene ring was found from the results of the calculation for molecules (IV) and (V).

The conformation corresponding to the energy minimum for all three molecules with substituents XMe_3 [(IV)—(VI)] has D_3 symmetry. A second possible conformation for these molecules, with S_6 symmetry, is much less favourable (by 16—18 kcal mol^{-1}).

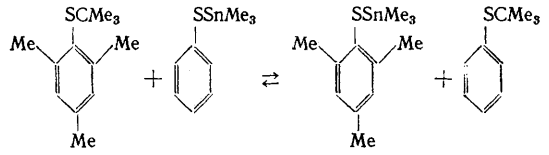
Molecules (I)—(III) have a large number of conformers [8 for (I) and 9 for (II) and (III)]. Calculation of their relative energies showed that for molecule (I), the most favourable conformation is that with D_{3d} symmetry (Me groups arranged alternately above and below the plane of the benzene ring), and for molecules (II) and (III) the C_{6h} conformation is most favourable (the H atoms of the substituent lie in the plane of the ring and occupy the space between the groups of neighbouring substituents). The calculation also made it possible to reach conclusions about the mechanism of internal rotation of the substituents in molecules (I)—(III). Two possibilities were examined—coupled (correlated) and "stepwise" (non-correlated) rotation of the ethyl, isopropyl, and dimethylsilyl groups. The second version of the rotation makes it possible to select the conformational transformation route with the lowest barrier. For example, for molecule (III), according to the calculations, the coupled rotation of the substituents can take place with an energy barrier of ~90 kcal mol^{-1}, whereas for stepwise rotation the barrier is ~35 kcal mol^{-1}. NMR data¶ for this compound give for the barrier the value $\Delta G \geqslant 22$ kcal mol^{-1}. Much better agreement is observed for the barriers to rotation of the substituents in molecules (I) and (II): 11.8 and 15.7 (calculation) and 11.5 and 14.2 (experiment) kcal mol^{-1} respectively. This proves the stepwise mechanism of internal rotation in molecules (I)—(III).

The optimum orientations and the barriers to internal rotation of the substituent R in molecules ArSR (R = CH_3, CMe_3, $SnMe_3$ and $SnPh_3$) have been compared.[42] The calculations showed that the substituent R usually does not lie in the plane of the aromatic

¶The energy of the internal rotation was measured by a dynamic NMR method for π-complexes of compounds (I)—(III) with $Cr(CO)_3$.[41] The authors cited[41] consider that the steric influence of tricarbonylchromium is slight, and that the conclusions about the mechanism of rotation in the isolated molecules C_6R_6 are unaffected.

fragment (the dihedral angle C–C–S–R is 80–90°). For Ar = Ph, internal rotation is possible for all the substituents except CMe_3. For Ar = Mes, this rotation is unlikely for all types of substituent.

The conformational energies of the starting materials and reaction products have also been calculated[42] for the exchange reaction:



The replacement of the t-butyl group, which experiences greater steric hindrance, by the trimethylstannyl group is accompanied by a decrease in the sum of U_{conf} for the reaction products compared with the sum for the starting materials by ~8 kcal mol^{-1}, that is the equilibrium should be displaced to the right.

The conformational characteristics of saturated molecules with one or several X atoms in the ring have been studied.[11,12,43,44] It is fairly obvious that these molecules should differ from the corresponding cycloalkanes, primarily because of the non-equivalence of the bond lengths in the ring. For silacyclopentane, the relative advantage of the conformers decreases in the order:[44]

half-chair (C_2) 8.42 kcal mol^{-1} → envelope (C_s) 11.77 kcal mol^{-1} →
→ planar conformation (C_{2v}) 14.23 kcal mol^{-1}

and the calculated values of the geometric parameters of the most stable conformer (C_2) agree with experimental data on its structure in the gas phase.[45] The introduction of methyl substituents into different positions in silacyclopentane (1-; 1,2-*cis*-; 1,2-*trans*-) does not lead to a significant change in its conformation.[44] When the ring does not contain a heteroatom (cyclopentane), the conformations C_2 and C_s are energetically equivalent.

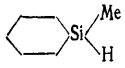
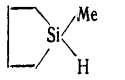
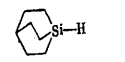
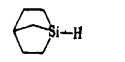
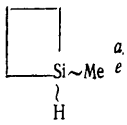
For silacyclohexane, the energy difference between the most favourable chair conformation and the next most favourable twist conformation (according to different data) is 3–4 kcal mol^{-1}.[11,43] For silacyclohexane, in contrast to cyclohexane, the ring is flattened slightly in the region of the Si atom and "wrinkled" in the region of the C atom lying opposite (according to calculation,[44] the endocyclic angles at these atoms are 104.2° and 113.5° respectively).

Comparison of the energies of mono-substituted silacyclohexanes[44] showed that for the 2-, 3-, and 4-methyl-derivatives, the equatorial isomers are more favourable (their energies are lower than those of the axial isomers by 1.87, 1.66, and 1.27 kcal mol^{-1} respectively). For 1-methylsilacyclohexane, the data on the relative advantage of the isomers differ slightly; Cartledge[44] considers the axial isomer to be more favourable, whereas Ouelette and co-workers[12] consider the equatorial isomer to be more favourable (difference in the energies 0.2 kcal mol^{-1} and 0.3 kcal mol^{-1} respectively). Both results indicate, however, that these isomers have similar energies.

For cyclic compounds of the type being considered, the calculations effectively reproduce the barriers to inversion of the ring. Thus for 1,1-dimethylsilacyclohexane, calculation gives the value 5.46 kcal mol^{-1}, and experiment gives the value 5.5 kcal mol^{-1} (in the analogous hydrocarbon, the corresponding values are slightly higher, 8.99 kcal mol^{-1} and 10–11 kcal mol^{-1}).

It has been shown[44] that the MMM can be used to establish the relationship between the structure and reactivity of compounds. The calculations were carried out for a series of cyclic and polycyclic molecules with one Si atom in the ring. It was previously assumed that in these compounds, the hydrolysis of the Si–H bond under basic catalysis conditions depends on the degree of strain of the coordination site including the Si atom, that is, in the language of molecular mechanics, on the contribution of U_{ang}(Si) to the total conformational energy. To verify this suggestion, the correlation between U_{ang}(Si) for several molecules and the hydrolysis rate constant was analysed (the corresponding data are given in Table 4 and Fig. 7). The graph in Fig. 7 shows that the strain in the angle at the Si atom is linearly dependent on lg k_{rel}, and the correlation coefficient (0.991) indicates that this relationship is not accidental.

Table 4. Strain in the angles at the Si atom and reactivity of a series of silanes in hydrolysis.[44]

Molecule, conformation	Endocyclic angles C–Si–C, °	U_{ang}(Si), kcal mol^{-1}	lg k_{rel}
 *a* *e*	104.6 104.9	0.4 0.4	0
	91.7	1.9	2
	102.2 102.2 102.2	2.1	2
	94.3 94.3 102.2	6.2	4
 *a* *e*	75.0 75.7	10.3 9.9	5.5

The study by experimental methods and calculations of the structure of cyclic and more particularly macrocyclic polysilanes is to a large extent determined by their unusual properties: the formation of charge-transfer complexes, radical-anions and radical-cations, and absorption in the ultraviolet range.[46]

A series of conformational calculations has been carried out[25,47] for cyclic silanes $(SiR_2)_n$ with small rings (n = 4–6) and different substituents, in particular with R = H, Me, Cl, Br, I. The authors cited compared the results of the calculations with earlier results obtained by calculations and experimental studies. The data obtained[25,47] are summarised in Table 5. Table 5 shows that for four-membered silane rings (as for cyclobutane), the folded conformation is more favourable. A similar result for $(SiH_2)_4$ was obtained by a non-empirical quantum-chemical calculation,[48] according to which the relative advantage of the D_{2d} conformation

Table 5. Relative conformational energy of cyclic silanes $(SiR_2)_n$, $n = 4-6$ (kcal mol^{-1}).

Molecule	Conformation (symmetry)	Substituents							
		H (Ref.24)	H (Ref.25)	Me (Ref.24)	Me (Ref.25)	Ph (Ref.47)	Cl (Ref.25)*	Br (Ref.25)*	I (Ref.25)*
$(SiR_2)_4$	folded (D_{2h})	—	0.0	—	—	—	0.0	0.0	0.0
	planar (D_{4h})	—	0.26	—	—	—	1.17	0.55	1.10
$(SiR_2)_5$	envelope (C_s)	0.01	—	0.0	—	—	0.0	0.02	0.0
	twisted (C_2)	0.0	—	0.0	—	—	0.0	0.0	0.05
	planar (D_{5h})	0.44	—	0.44	—	—	2.08	3.54	4.90
$(SiR_2)_6$	chair (D_{3d})	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	twisted boat (D_2)	1.96	2.22	2.34	2.89	18.90	1.58	2.10	2.65
	boat (C_{2v})	2.32	2.49	3.83	4.14	—	2.34	3.47	4.88
	twisted (C_2)	4.14	3.49	4.11	4.23	—	3.44	2.34	5.07
	envelope (C_s)	—	3.80	—	4.52	—	3.71	5.65	5.62

*Calculation carried out with allowance for the electrostatic component.

compared with the D_{4h} conformation is 0.54–0.74 kcal mol^{-1} (calculations in different basis sets). This difference in energy indicates conformational non-rigidity of the four-membered silane rings. The conformational non-rigidity of four-membered silane rings is also indicated by experimental data. Thus according to XRD data, the molecules of $(SiMe_2)_4$ [49] and $[Si(SiMe_3)_2]_4$ [50] are planar, and the molecules of $[Si(i\text{-}Pr)_2]_4$,[51] $[SiMe(Bu\text{-}t)]_4$,[52] and $(SiPh_2)_4$ [53] are folded; the angles of bending in the last three molecules are 37.1, 37.0, and 12.8° respectively. For the last two molecules, calculation using the MMM [47] led to good agreement between the experimental and calculated geometric parameters.

For cyclopentasilanes with different substituents, as for cyclopentane, the two conformers C_s and C_2 have similar energies. For the Ph-derivative, whose structure was studied in the crystal, an intermediate conformation was found.[54]

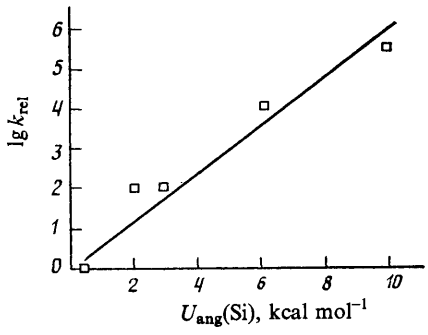


Figure 7. Dependence of lg k_{rel} for the hydrolysis of the SiH group on the strain in the valence angles at the Si atom.[44]

The optimum conformation of cyclohexasilane and its derivatives is the chair conformation, in agreement with experimental data for $(SiH_2)_6$ (GED),[55] $(SiMe_2)_6$ (XRD),[56] and $(SiMePh)_6$ (XRD).[57] According to calculations[24,58,59] and GED data,[55] the cyclohexasilane molecule is less flattened than the cyclohexane molecule [the valence angles in the $(SiH_2)_6$ and $(CH_2)_6$ rings are 111.4° and 110.3° respectively, and the torsional angles are 54.9° and 57.9°]. This is understandable, since the bonds in the ring in the $(SiH_2)_6$ molecule are appreciably longer than those in the $(CH_2)_6$ molecule, so that the repulsion of the groups occupying the *gauche*-positions will be smaller in $(SiH_2)_6$ than in $(CH_2)_6$ (by analogy with the non-cyclic tetrasilane).

For the seven-membered cyclosilane $(SiMe_2)_7$, according to XRD data and calculation,[60] the characteristic conformation is the twisted chair (*TC*) conformation. The same conformation is also the most favourable for cycloheptane. The calculation showed, however, that the relative advantage of other conformers† (Table 6), and also the conformational transformation routes, are different for $(SiMe_2)_7$ and its hydrocarbon analogue.

Even greater structural and energetic differences compared with the hydrocarbon analogues were observed[61] for the $(SiMe_2)_8$ molecule. This is obvious from a comparison of the conformational energies (kcal mol^{-1}) of a number of conformers:

	TCC	*CC*	*CR*	*TBC*	*BC*	*TB*	*TC*	*C*	*BB*	*B*
$(SiMe_2)_8$ (Ref.61)	0.0	0.4	0.9	2.3	2.6	3.7	4.3	6.3	9.2	10.7
$(CMe_2)_8$ (Ref.62)	—	—	1.22	2.37	0.0	—	9.96	9.51	1.67	12.13

†The torsional angles and the generally accepted notation for the conformers of cyclic molecules (*C* = chair, *B* = boat, *TC* = twisted chair, *TB* = twisted boat, *CR* = crown, *BB* = boat–boat, *CC* = chair–chair, *TCC* = twisted chair–chair, *TBB* = twisted boat–boat, etc.) have been described in detail.[63]

The authors cited[61] also noted a significant increase in the valence angles in the ring at the Si atoms (118–123°), which exceed the equilibrium value (111.7°); the same was previously observed for $(SiMe_2)_7$.[60] Thus with increase in the size of the ring, the differences in the structures and conformational behaviour of the molecules of cyclic silanes and the corresponding hydrocarbons increase.

Table 6. Relative energy (kcal mol^{-1}) of the conformers of $(SiMe_2)_7$ and $(CH_2)_7$.[60]

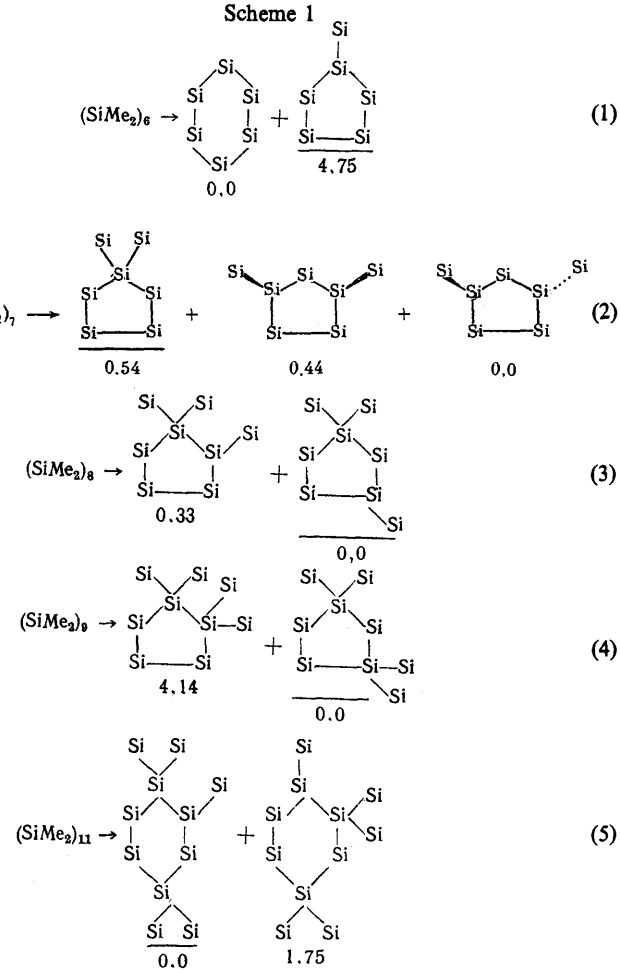
Conformer	$(SiMe_2)_7$	$(CH_2)_7$ *
TC	0.0	0.0
C	0.9	0.63–1.58
TB	2.6	2.40–5.64
B	4.2	2.60–5.66
TT	2.9	8.1–9.6

*The scatter in the data of different authors cited by Shafiee[60] are given.

Molecules with larger ring dimensions have been less extensively studied. Data have been published[64] on the structures of the molecules $(SiMe_2)_{13}$ and $(SiMe_2)_{16}$ in the crystals. Comparison of their conformations with those of their hydrocarbon analogues, in which the ring most frequently can be "placed" in the diamond lattice, shows appeciable differences in both cases. A calculation of the geometric characteristics of hypothetical conformers of the $(SiMe_2)_{13}$ molecule with the "pentagonal" or "trigonal" conformations (the conformer consists of five or three approximately planar fragments), observed for the hydrocarbons $(CR_2)_{13}$, showed that these conformations cannot be produced in the case of the cyclosilane, since they lead to shortened contacts between the methyl groups. The values of the torsional angles in the $(SiMe_2)_{13}$ and $(SiMe_2)_{16}$ rings differ considerably from the values corresponding to the *trans*- and *gauche*-arrangements of the units, indicating again that the silanes have a greater conformational flexibility than the hydrocarbons.

In the standard version of the MMM, electronic effects (for example conjugation) are not taken into account in explicit form. This makes it possible to use the mechanical model to detect those cases where the part played by electronic effects (irrespective of their nature) is considerable. An example of this use of the MMM is provided by studies[58,59] of a large group of alkyl-substituted penta- and hexasilanes. These compounds are products of the isomerisation of permethylated cyclic silanes $(SiMe_2)_n$ with $n = 5-11$, and a characteristic feature of the reaction, which takes place in the presence of the catalyst $AlFeCl_6$, is that the isomerisation of each of the rings usually gives a product consisting of a single isomer (Scheme 1). Scheme 1 shows only the energetically most favourable isomers (the Me groups are not shown). The values of ΔU_{ster} (kcal mol^{-1}) are given. The isomers whose yields are 95% are underlined.

Scheme 1



It is suggested that in these reactions, decrease in the ring size leads to a gain in the so-called σ-conjugation energy‡. The σ-conjugation energy for the molecules being considered can be estimated as follows. The gain in free energy for the isomer formed is written as the sum

$$\Delta H = \Delta H_{ster} + \Delta H_{bd} + \Delta H_{\sigma}.$$

Data on the ratio of the isomers (reaction products) make it possible to estimate ΔH, the MMM can be used to calculate ΔH_{ster}, and the value of ΔH_{bd} (a characteristic of the bonds in the molecules) is assumed[58,59] to be the same for all the isomers. These quantities can then be used to calculate ΔH_{σ}.

For $(SiMe_2)_6$ (Scheme 1), the ratio of the initial and final isomers is 99:1, which gives for ΔH the value 2.7 kcal mol^{-1}. With allowance for the difference ΔH_{ster} indicated in the Scheme, ΔH_{σ} for this pair of isomers is 7.4 kcal mol^{-1}, that is in this case the formation of the product with the five-membered ring is determined by not steric but electronic factors. The same is characteristic of the isomers obtained from $(SiMe_2)_7$; in this case, ΔH_{σ} is 3.2 kcal mol^{-1}.

For the products of the isomerisation of 8-, 9-, and 11-membered cyclosilanes, the preference for the formation of a given isomer is determined by steric factors. Summarising the results of calculations

‡The concept of σ-conjugation has been discussed in detail.[65]

and the experimental study of the ratio of the quantities of isomers obtained, the authors cited[58,59] point out that in the formation of cyclic isomers with the same number of silicon atoms in the ring and different arrangements of the $SiMe_3$ substituents, a decisive role in the "choice" of product is played by steric factors [see reactions (3)–(5) in Scheme 1]. When the numbers of silicon atoms in the ring or the positions of the substituents are different [reactions (1) and (2)], the electronic σ-conjugation effect predominates.

In the opinion of the present authors, however, no absolute significance should be given to the separation of the contributions into steric and electronic (this is indicated by a detailed quantum-chemical analysis of these contributions in four- and five-membered cyclosilanes[48]). These conformational calculations also lead to the conclusion that the force field suitable for the description of cyclosilanes with $n \geqslant 6$ should not be extended automatically to the description of smaller rings.

The range of substances which have now been examined using the MMM includes compounds containing the bonds X–O, X–N, X–S, etc., such as organoelemental peroxides, siloxanes, and silazanes.

Siloxanes. The MMM has been applied to the organosiloxanes,[66,67] an extensive class of compound with wide practical applications in polymer chemistry.[68] The selection of the required parameters of the potentials describing the siloxane bond has been carried out for various simple linear and cyclic siloxanes: $(H_3Si)_2O$, $(Me_3Si)_2O$, $(Me_2SiO)_3$, $(H_2SiO)_4$, and $(Me_2SiO)_4$.[66] These parameters supplement the set of parameters proposed by Allinger and Tribble[11] for the description of the molecules of silanes and carbosilanes.

A detailed analysis of the conformational possibilities of the tetrasiloxane ring, which is the basic structural fragment of a number of polymers, has been carried out.[67,69] An eight-membered ring with fixed bond lengths and valence angles has two degrees of freedom,[70,71] namely two torsional angles, and the values of the remaining six torsional angles are determined by the ring closure conditions.[72] A calculation for non-substituted cyclotetrasiloxane[69] showed that in the space of the two independent torsional angles (φ_1 and φ_2), the extensive range shown in Fig. 8 is allowed (within the isoenergetic line 10 kcal mol^{-1}). The values of the remaining torsional angles also lie in this range.

The tetrasiloxane ring is much more flexible than the cyclo-octane ring;[69] a typical value of the difference between the energies of the symmetrical conformers§ is 0.1–0.2 kcal mol^{-1}, and the least favourable planar conformer differs from the most favourable conformer by only 3.4 kcal mol^{-1}. It was also shown that for a given conformation, a smooth change in the torsional angles without an appreciable change in energy is possible. The small difference in the conformational energies is associated with a large variety of unsymmetrical structures of the tetrasiloxane ring observed in the crystals;[74] these structures can be represented approximately as the superposition of the symmetrical canonical forms of the eight-membered ring. The conformational non-rigidity of the siloxane molecules is apparently one of the reasons for the greater "friability" of siloxane crystals compared with organic molecular crystals.[75]

A smaller siloxane ring (cyclotrisiloxane) compared with the tetrasiloxane ring is characterised by the single energetically most favourable planar conformation.[66]

§The canonical symmetrical forms of the eight-membered rings according to Hendrickson[63,73] were examined.

According to XRD data[76] and calculation,[76] in the carboxysiloxane six-membered ring of the $CH_2CH(COOH)CH_2SiMe_2OSiMe_2$ molecule the siloxane fragment CSiOSiC also remains planar, whereas the CCC angle deviates from this plane by 57°, that is the ring as a whole has the "sofa" conformation.

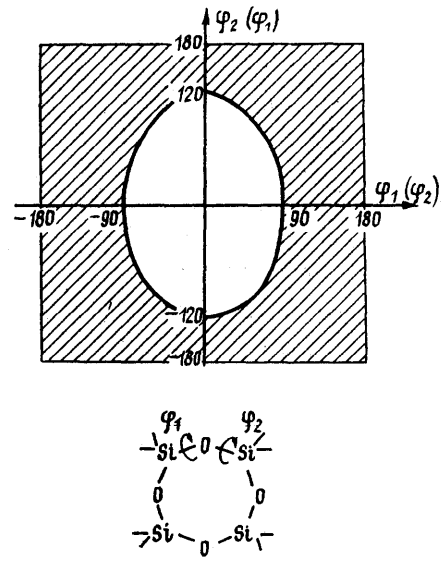
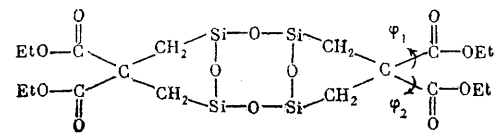


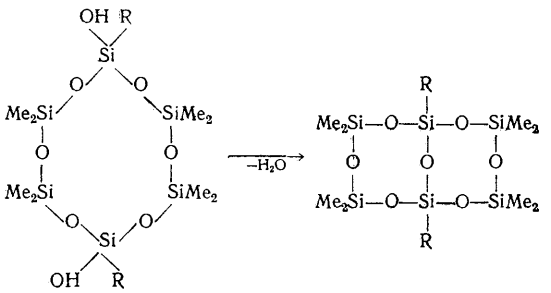
Figure 8. Range of existence of cyclotetrasiloxane in the space of the torsional angles φ_1 and φ_2 (the forbidden region is hatched).[69]

For various organosiloxanes, calculations have established the relationship between the conformational characteristics of the molecules and their chemical behaviour. Thus in the tricyclic molecule



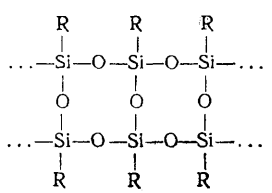
the pseudo-equatorial ester group can undergo practically free rotation (angle φ_1), whereas for the pseudo-axial group there are two ranges of allowed values of φ_2 close to ~60° and ~240°, separated by a high barrier.[77] The orientation of the pseudo-axial group in the crystal (φ_2 = 60°[77]) lies in one of the allowed ranges, and should not change on transfer to solution. This ester group occupies a shielding position relative to the carboxysiloxane group and, partly, the siloxane ring, and this (together with the redistribution of charges on the atoms of the ring, taking place under the influence of the ester substituent) probably explains the lowered reactivity of this compound in ionic splitting reactions.

The possibilities of change in the conformation of a twelve-membered siloxane ring on dehydration, taking place with the formation of a bicyclic product, have been examined.[78,79]



According to the calculation, in the ring with the *cis*-arrangement of the OH groups the approach of these groups is possible without a significant change in U_{conf} for the molecule to a distance corresponding to the formation of an H-bond between them (O...O ~ 2.94 Å). Dehydration at this bond apparently gives the bicyclic product. For the *trans*-isomer, this approach is impossible, and the formation of a cyclic product can take place only with rupture of the bonds in the ring at intermediate stages of the reaction. The conformation of the molecule of the *cis*-isomer predicted in the work cited[78] showed good agreement with that subsequently found in the crystal,[80] where the ring again has the boat form, and the OH groups are joined by an intramolecular H-bond (O...O 2.71 Å).

The bicyclic product obtained in the reaction is the simplest fragment of the cyclic–linear ladder polymer



A calculation[67] carried out for the bicyclic molecule showed that for it, at least two conformations with similar energies are possible (in the first, the molecule has C_2 symmetry, and both rings have the *BB* conformation, and in the second, one ring has the *CB* conformation, and the other the *LC* conformation), differing from the conformation found in the crystal.[81]

For the molecules of oligomers containing three cyclic fragments, where the side rings are joined in *cis*- and *trans*-fashion to the central ring, the calculated geometric parameters (particularly for the central ring) show fairly good agreement with those obtained by XRD.[74,82] These results indicate that introduction into the bicyclic molecule does not restrict the mobility of the eight-membered siloxane rings, whereas tricyclic (and hence polycyclic) connection makes this ring fairly rigid.

The calculation also showed slight energetic preference for *trans*-connection for the tricyclic molecule, compared with *cis*-connection (8.17 kcal mol^{-1} and 7.55 kcal mol^{-1} respectively). This indicates that for the ladder polymer, the *trans*-connection of the rings (Fig. 9*a*) is more favourable than alternate *trans*- and *cis*-connection (Fig. 9*b*).

In the above studies, the structure of the polymer chain was estimated from the results of calculations for its fragments represented by oligomer molecules. Other authors[83–85] examined the structure of infinite linear siloxane chains $(R_2SiO)_n$ in the isolated state and in the crystalline regions of the polymer. The calculation for the isolated chains $(R_2SiO)_n$, where R = Me, Et, Pr,[83] and Ph [85] showed that the spiral conformation is energetically most favourable. For polydimethylsiloxane, several possible conformations were examined, corresponding to the planar zigzag and the spirals 4_1 and 6_1 (with four and six units in each period). The spiral 4_1 version was found to be energetically most favourable, but the difference between its energy and that of the next most favourable version 6_1 is small (energy difference ~0.1 kcal mol^{-1}), while the production of the planar zigzag conformation is unlikely. For the molecules of polydiethyl- and polydipropylsiloxanes, several conformations of similar energy were detected, having approximately the same spiral step (~2.35 Å) but differing in the orientation of the substituents and the angle of rotation about the virtual bond O...O characterising the connection of the chain units. The final selection of the most favourable conformation in these cases made it possible to carry out a search for the optimum packing of the molecules in the crystal, corresponding to a minimum value of $U_{conf} + U_{interm}$, where the last term characterises the intermolecular non-valence interactions.[84] The search for this packing was carried out using the space groups and unit cell parameters obtained in an X-ray diffraction study of the crystalline polymers. For the tetragonal polydipropylsiloxane and the monoclinic polydiethylsiloxane, the most favourable conformation in the crystal is the spiral with 4_1 symmetry.

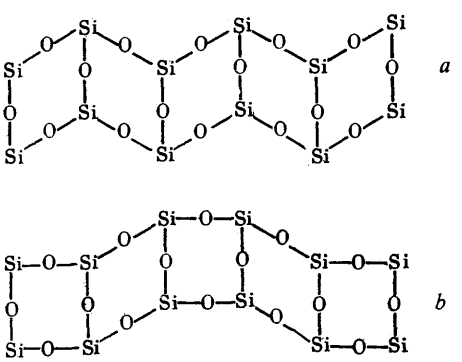


Figure 9. Cyclic–linear polyorganosiloxanes with *trans*- (*a*) and *cis*–*trans*- (*b*) connection of the rings.

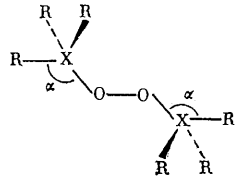
The same conformation is characteristic of polydiphenylsiloxane in the free state and in the crystal.[85] In the last case the authors cited note that the conformation is the same in the two states mentioned. Thus for all the polyorganosiloxanes examined (at least in the crystalline state), the most favourable conformation is the spiral 4_1, with slight differences which are due to the increase in the volume of the substituents and which correspond to an increase in the spiral step and in the valence angles at the O atoms.

Peroxides. The conformational characteristics of organosilicon and organic peroxides with similar structures have been examined.[86–89] A common feature of the molecules of simple peroxides is the "half-opened book" conformation with torsional angle ω about the O–O bond equal to 90–150°. For molecules

with bulky organoelemental and organic substituents, this angle may reach 180°, that is the molecule as a whole has the *trans*-conformation.

The conformations of a series of peroxides $Me_2RSiOOSiRMe_2$, where R = Me, CH_2Ph, and *p*-C_6H_4Cl, have been calculated.[86] The values of the angle ω in these compounds are 143.5° (GED),[90] 180°, and 180° (XRD)[88] respectively. The aim of the calculation was to determine whether the *trans*-conformation in the last two compounds is due to the effect of the crystalline environment, or whether it is characteristic of these molecules in the free state. It was found that for the molecule with R = Me, the optimum angle is ω = 140°; for the molecule with the slightly larger substituent R = CH_2Ph, two ranges of favourable conformations corresponding to angles ω = 140° and 180° were detected, the energy of the first being lower by 0.7 kcal mol^{-1}; and, finally, for the molecule with R = *p*-C_6H_4Cl the only favourable conformation is the *trans*-conformation (ω = 180°). Thus the molecule of the peroxide with R = CH_2Ph apparently adopts the *trans*-conformation under the influence of the crystal field. With more bulky substituents, this conformation is also characteristic of the isolated molecule. The same regularities were found in calculations for the molecules of organic peroxides R_3COOCR_3.[87,89]

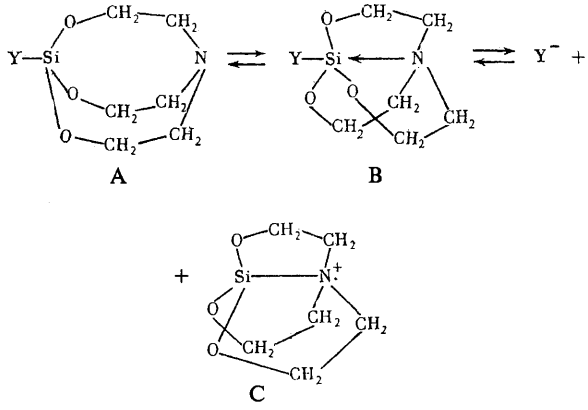
The MMM does not reproduce all the characteristics of the structure of peroxide molecules. X-Ray diffraction[87–89] has shown that in organic and organoelemental peroxides



the value of the valence angle O–X–R (α), including the X–R bond in the *trans*-orientation to the O–O bond, is always smaller than the tetrahedral value, and equal to ~100°. It has been shown[89] that the tendency for this angle to decrease is not reproduced satisfactorily in calculations using the MMM, but is effectively described by the semi-empirical CNDO/2 quantum-chemical method, indicating that this effect is predominantly electronic.

In the molecules of $Me_3COOCMe_3$ and $Me_3SiOOSiMe_3$, GED [90] did not detect a decrease in the angle α, whereas X-ray gave for the first molecule a value of α equal to 100.7°.[89] This difference is due to the fact that the GED refinement was carried out using a model with fixed symmetry of the Me_3X groups (C_{3v}),[90] which could not have led to a decreased value of one of the valence angles.

Silatranes. As noted in the Introduction, the range of applicability of the MMM is usually restricted to those cases of change in the structure of molecules where there is no rupture or formation of chemical bonds. Earlier, however, attempts had already been made to modify the mechanical model in order to examine processes of molecular rearrangement accompanied by a change in the coordination of various atoms, that is essentially not conformational but chemical transformations. An example from organoelemental compounds is provided by studies[91–94] in which a method for carrying out these calculations was developed for the case of the 1-methylsilatrane molecule. The last of the works cited,[94] in which the most fully developed calculation procedure was used, can be considered in more detail. The authors cited examined the hypothetical conversion of the energetically unfavourable *exo*-form of the silatrane A into the ionic product C, which is also unfavourable, via the *endo*-form B, which is the only one to actually exist:



The authors cited[94] regard this process as a model substitution reaction of the S_N2 type. To take account of the change in the coordination number of the silicon atom, the dependence of the equilibrium values and force constants of the valence angles on the bond orders (*P*) at the Si atom was introduced into the model. The nature of the change in the bond orders in this reaction was the subject of a special study;[95] in particular, in the *exo*-form $P_{Si-N} = 0$, and in the *endo*-form $P_{Si-N} = P_{Si-Y}$.

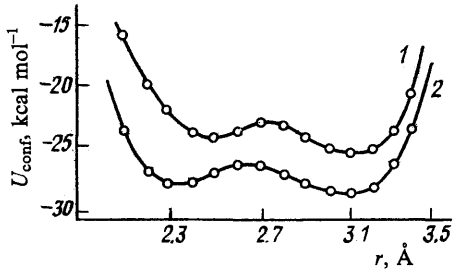


Figure 10. Dependence of the conformational energy on the distance Si...N for the molecules of 1-methylsilatrane (*1*) and 1-chlorosilatrane (*2*).

The calculated dependence of the energy (U_{conf}) on the distance Si–N (reaction coordinate) for the molecules with Y = Me and Cl is shown in Fig. 10. Curves *1* and *2* have minima corresponding to the *endo*-form which actually exists, and to the *exo*-form which has not been detected; the geometric parameters of the first show good agreement with those found for molecules of this kind by GED and XRD. The calculation showed that with the usual parametrisation (tetrahedral coordination of the silicon atom), these curves will have only one minimum, corresponding to the *exo*-form.

The authors cited[95] point out that the differences in the energies of the forms and the barriers to the transformation calculated for both molecules do not explain the fact that the silatrane molecules

exist only in the *endo*-form and the fact that quantitative agreement between calculation and experiment can be achieved only by taking account of the energy of the hypervalent bonding Y—Si ← N. In spite of these shortcomings, the results obtained are fairly encouraging, since they make it possible to obtain geometric parameters of the molecules which are close to the actual values, at the point corresponding to the minimum on the reaction coordinate.

IV. Conformational calculations for organometallic molecules

The previous section examined molecules in which the atom X has a definite (most frequently four-fold) coordination, analogous to the coordination of the C atom (sp^3) in organic molecules; this made possible an exhaustive description of its immediate environment using the X—R bond lengths and valence angles. The examination of structural data on the nature of the ligand environment of a metal atom (M) in organometallic complexes (mononuclear and polynuclear π-complexes and metal clusters) shows that in these compounds there is no rigidly fixed coordination of the M atom,[96,97] so that it cannot be described in terms of ideal values of the valence angles at the M atom. This feature, and also the widely encountered view that the structure of these molecules is determined chiefly by electronic factors, apparently explain why, until recently, there has been practically no application of the mechanical model to the examination of organometallic molecules¶.

1. Mononuclear metal complexes

Until recently, the only example of the application of the MMM to π-complexes was that described by Dashevskii and co-workers.[98] For molecules of the type $(C_5H_5)_2M$, the authors cited calculated the dependence of the energy of the non-valence inter-ligand interaction on the angle of relative rotation of the parallel cyclopentadienyl (Cp) rings. In agreement with the experimental data, it was shown that the barrier to this rotation is low, and that, depending on the M—C(Cp) distance, the molecule may have the staggered ($\varphi = 36°$, $d \lesssim 2.05$ Å) or eclipsed ($\varphi = 0°$, $d > 2.05$ Å) conformation of the ligands. A calculation has also been carried out for the $(C_5H_5)_2TiCl_2$ molecule, assuming ideal tetrahedral coordination of the Ti atom.[98] The minimisation of U_{conf} gave a ligand arrangement agreeing with that obtained by electron diffraction (the angle Cl—Ti—Cl is 105° or 102°, and the dihedral angle between the Cp ligands 125° or 121°, according to calculation and GED respectively).

Later, a simplified version of the MMM was proposed,[100–102] which makes it possible to predict fairly reliably the geometric characteristics of π-complexes. This model of a mononuclear π-complex ("hinge" model) is based on the view that the coordination sphere of the metal is uniformly occupied by the ligands,[99,103] and the criterion of uniform filling is the attainment of a minimum energy of the non-valence inter-ligand interaction. In this case the geometric characteristics of each of the organic ligands are calculated using the usual MMM scheme; the constants characterising the rigidity of the valence angles at the metal atom are taken as zero, and the metal—ligand distances are fixed by specifying high values of the deformation constants of the bond lengths M—L.

For a comprehensive verification of the proposed model, π-complexes of three main types were examined:[101,102,104] a, the half-sandwich compounds $CpM(CO)_3$ (Fig. 11*a*); b, the sandwich compounds $(C_5R_5)_2M$ with R = H or Me (Fig. 11*b*); and c, wedge-sandwich compounds with additional ligands $(C_5R_5)_2ML_n$, where L = H, Cl, CO (Fig. 11*c*). For the half-sandwich molecules, the calculation was carried out for values of the bond lengths M—Cp (centre of gravity of the Cp ligands) equal to 1.730 Å and 1.957 Å, and values of the M—CO bond lengths equal to 1.826 Å and 1.894 Å, characteristic of metals of the first and second transition series. The calculated values of the inter-ligand angles α (Fig. 11*a*), equal to 95.2—96.4° for the first set of distances and 98.7—99.7° for the second, show good agreement with XRD data for $CpMn(CO)_3$ [105] (M—Cp 1.79 Å, M—CO 1.79 Å, α = 91—94°), $[CpFe(CO)_3]^+PF_6^-$ (M—Cp 1.68 Å, M—CO 1.82 Å, α = 92—95.6°), and $CpRe(CO)_3$ (M—Cp 1.96 Å, M—CO 1.90 Å, α = 89.9—90.5°). Increase in the covalent radius of the atom M leads to a decrease in the steric strain in the coordination sphere and to slightly less satisfactory quantitative agreement between the calculated and experimental values of the angles α, although qualitatively the geometry of the "piano stool" is reproduced correctly.

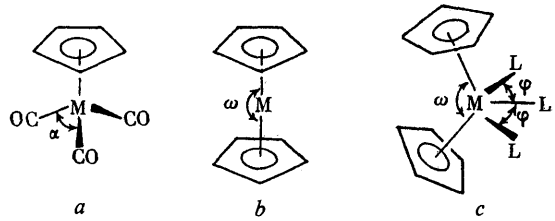


Figure 11. Types of π-complex studied:[101,102] *a*, half-sandwich $CpM(CO)_3$; *b*, sandwich $(C_5R_5)_2M$; and *c*, wedge-sandwich with additional ligands $(C_5R_5)_2ML_n$.

A calculation[102] carried out for the half-sandwich complex $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ (Fig. 12) effectively reproduced all the experimentally observed structural characteristics.

In sandwich molecules with the parallel arrangement of the CP ligands, the inter-ligand contacts C...C are usually close to the normal van der Waals distances, so that regular filling of the coordination sphere of the metal atom is observed. At the same time, the structures of a number of bis-cyclopentadienyl derivatives Cp_2M, where M = Si, Ge, Sn, Pb, As,[106–109] have molecules with a wedge-sandwich configuration. According to quantum-chemical calculations, this arrangement of the Cp rings is due to the presence of a localised lone pair of electrons of the atom M in the equatorial plane of the wedge-sandwich.[106] An alternative explanation of the

¶The MMM is applied fairly extensively[7] to the molecules of coordination compounds in which the values of the valence angles at the M atoms are fixed. At the same time, in coordination chemistry, use is also made of models in which the most favourable arrangement of the ligands is determined by the minimum of the energy of interaction of points arranged on a sphere and approximating the ligands.[99]

wedge-shaped arrangement of the rings[101,102] takes account of only the non-valence inter-ligand interaction, and corresponds to the mutual attraction of the Cp ligands, where the non-valence contacts between the ligands when M has a large radius correspond to an attractive van der Waals interaction.

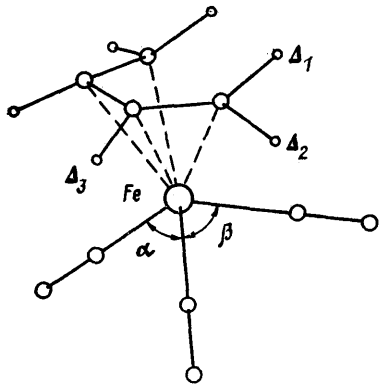


Figure 12. Structure of the $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ molecule; the geometric parameters have the following values: α = 93.7° and 92.0°, β = 98.3° and 100.0°; Δ_1 = 0.65 Å and 0.50–0.65 Å, Δ_2 = −0.14 Å and from −0.15 Å to −0.20 Å, Δ_3 = −0.48 Å and from −0.05 Å to −0.15 Å from calculation and experiment respectively (Δ is the deviation of the hydrogen atom from the average plane of the ligand).[102]

A calculation[101] of the optimum configuration of metallocenes, characterised by the angle ω (see Fig. 11*b*), in the range of distances M–Cp from 1.6 Å to 2.5 Å at intervals of 0.05 Å showed preference for the wedge-sandwich configuration for the molecules Cp_2M and $(C_5Me_5)_2M$ for distances M–Cp greater than 1.80 Å and 2.05 Å respectively. Qualitative agreement was observed between the calculated and experimental values of the geometric parameters in these molecules (Fig. 13). The slight quantitative differences[101,102] are attributed to the appreciable conformational flexibility of the wedge-shaped sandwich, and hence to the influence of the crystal field on its geometry, found by XRD. This effect is illustrated, for example, by the difference in the angles ω in the Cp_2Sn molecule in the gas phase (GED) and in the crystal (XRD) and by the coexistence in the $(C_5Me_5)_2Si$ crystal[109] of two symmetrically independent molecules with markedly different angles ω, equal to 180° and 154.7°. The model used also effectively explains the increase in the angle ω when bulky substituents are introduced; the experimental values of this angle in Cp_2Sn[106] (GED), $(C_5Me_5)_2Sn$,[105] and $(C_5Ph_5)_2Sn$[110] are 125, 144, and 180°; and in Cp_2Ge[108] and $[C_5H_2(SiH_3)_3]_2Ge$[111] 129.6° and 171° respectively. Thus in the approximation used (and in agreement with experiment) it has been shown that with increase in the radius of the atom M, the structure of the metallocene molecule changes from parallel to wedge-sandwich under the influence of van der Waals forces.

For wedge-sandwich metallocene derivatives with additional ligands, where there is more "compact" filling of the coordination sphere of the metal by the ligands, better agreement between the calculated and experimental values of the angles at the central atom M should be expected. This is confirmed by the data in Table 7, where the calculated and experimental values of the angles ω and φ are compared (see Fig. 11*c*). The experimentally observed decrease in the angle φ on going from the complexes with the d^0 electron configuration of the atom M to the d^1 and d^2 complexes is satisfactorily explained in the MMM by steric factors, although usually this change in the geometry is interpreted on the basis of the molecular-orbital model as the result of the electrostatic repulsion of the ligands in the bisector plane and the electrons localised in the "rear" orbitals of the metal atom.[112] Here, the difference between the calculated and experimental values of the angles is small for φ, and slightly greater for ω. This result shows that calculations using the MMM can be used to reproduce qualitatively fairly fine structural effects previously attributed to electronic factors.

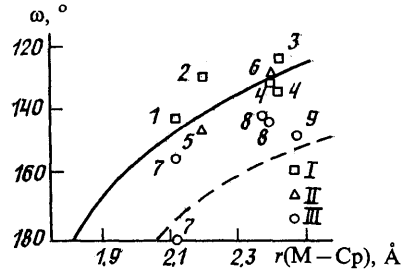


Figure 13. Calculated dependence of the angle ω on the distance M–Cp in Cp_2M (continuous line) and $(C_5Me_5)_2M$ (broken line); I, experimental values for Cp_2M molecules; II, the same for $(C_5H_4Me)_2M$; III, the same for $(C_5Me_5)_2M$; *1*, Cp_2As (XRD);[107] *2*, Cp_2Ge (XRD);[108] *3*, Cp_2Sn (GED);[106] *4*, Cp_2Sn (XRD, two independent molecules);[106] *5*, $(C_5H_4Me)_2Ge$ (GED);[106] *6*, $(C_5H_4Me)_2Sn$ (GED);[106] *7*, $(C_5Me_5)_2Si$ (XRD, two independent molecules);[109] *8*, $(C_5Me_5)_2Sn$ (XRD, two independent molecules);[106] *9*, $(C_5Me_5)_2Pb$ (XRD).[106]

These results[101,102,104] show the possibilities provided by the study of organometallic π-complexes by the MMM method, whose development should apparently take the direction of a search for an improved parametrisation.

Here, mention may be made of another purely geometric model, whose conceptual basis is similar to that of the method examined above, and which also makes it possible to obtain the characteristics of the coordination environment of the metal atom in the molecules of π-complexes. This model is based on Tolman's approach,[113] which makes it possible to describe the filling of the coordination sphere of the metal atom using the body (conical) angles characterising the projection of the ligand on to the coordination sphere of the metal. An analysis[114] of a large number of examples, including lanthanide π-complexes, was used to formulate the "packing centre" rule, according to which the sum of the products of the fraction of the body angle corresponding to the ligand and the length of the vector characterising the relative position of the ligand is close to zero. This rule makes possible an *a priori* quantitative description of the relative arrangement of the ligands in mono- and

dinuclear complexes with a sufficiently high accuracy. The authors cited point out that this rule is analogous to the requirement of a minimum energy for the non-valence interaction of the ligands in their optimum arrangement.

Table 7. Calculated[101] and experimental[105] values of the geometric parameters of molecules of the type $(C_5R_5)_2ML_n$.

Compound	M–Cp, Å	M–L, Å	φ, °		ω, °	
			calc.	exper.	calc.	exper.
Cp_2NbH_3	2.06	1.70	73.7	63	138.5	141.5
Cp_2TaH_3	2.07	1.77	71.8	62.9	139.1	139.9
Cp_2ZrCl_2	2.20	2.44	94.7	97.2	134.0	127.0
Cp_2TiCl_2	2.12	2.36	90.4	95.2	135.3	129.1
Cp_2NbCl_2	2.09	2.47	86.9	85.6	138.3	130.5
$[Cp_2MoCl_2]^+$	1.99	2.39	83.1	87.9	140.0	131.5
Cp_2MoCl_2	1.98	2.47	81.9	82.0	141.4	130.5
Cp_2MoH_2	1.94	1.69	81.0	75.5	139.3	145.8
$Cp_2Ti(CO)_2$	2.03	2.03	86.9	87.9	133.4	138.6
$Cp_2Zr(CO)_2$	2.18	2.19	82.5	89.2	132.9	143.4
$[Cp_2V(CO)_2]^+$	1.92	1.96	88.6	92	131.1	137.9
$(C_5Me_5)_2Ti(CO)_2$	2.07	2.01	82.2	83.3	146.1	147.9
$(C_5Me_5)_2Zr(CO)_2$	2.20	2.15	80.3	86.3	147.4	147.4
$(C_5Me_5)_2Hf(CO)_2$	2.17	2.14	81.6	87	146.1	148.2

the immediate environment of the metal atom but the relative arrangement of the parts of the complex or the orientation of the substituents in the ligands. In these cases, when carrying out a conformational analysis, the coordination environment is most frequently fixed, and only a limited number of the parameters being considered are varied. Examples of such calculations, which were begun only recently, have been published.[115,116]

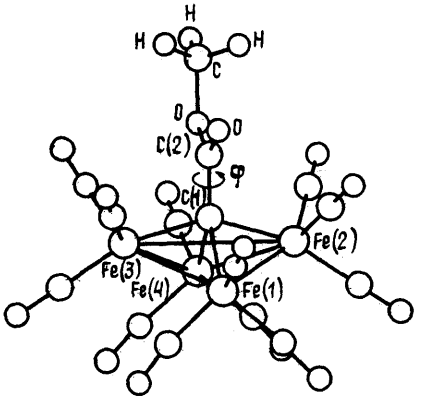


Figure 14. Structure of the $Fe_4(CO)_{12}CC(O)OCH_3$ molecule.[115]

In the opinion of the present authors, this rule should be fulfilled effectively only for sufficiently "compact" filling of the coordination sphere by ligands (for example, for the molecules MCp_3, where M represents a lanthanide, examined in the work cited[114]). It is fairly obvious that in the wedge-shaped sandwich molecules of the same lanthanides (for example for the wedge-sandwich $SmCp_2$ and $EuCp_2$) this rule is not fulfilled, but the conformation of these molecules is effectively described using the hinge model mentioned above.

In a number of cases, in the examination of the conformation of the molecules of mononuclear and polynuclear π-complexes, the feature of particular interest is not the arrangement of the ligands in

In the first of the works cited, U_{conf} was calculated to establish the relationship between the nature of the substituent R = COOMe, CH_2, and Me and the reactivity of the iron cluster $Fe_4(CO)_{12}CR$, which has the "butterfly" shape (Fig. 14). For R = COOMe (the structure of this cluster has been established experimentally by XRD[115]), the calculated orientation of the substituent showed good agreement with experiment. A similar position of the substituent was found in the model molecule with R = CH_2. For the cluster with R = Me, the total conformational energy is many times greater than that for R = CH_2, because of the short contacts between the hydrogen atoms of the CH_3 group and the carbonyl ligands. This

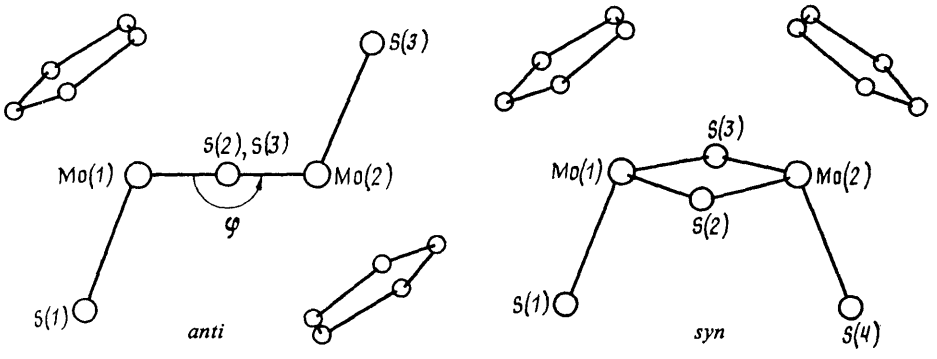


Figure 15. *syn*- and *anti*-forms of the molecules $[(C_5R_5)MoS(\mu\text{-}S)]_2$, where R = H, Me.[116]

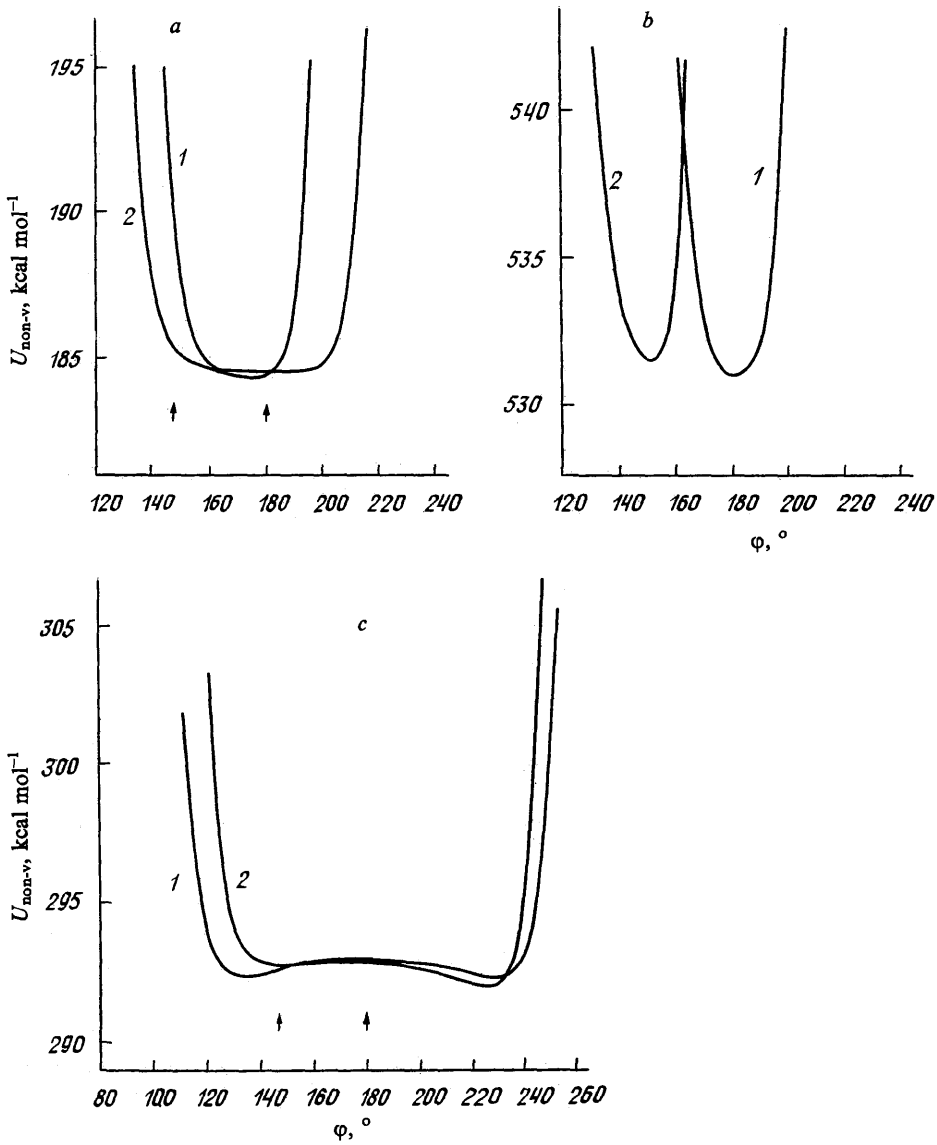


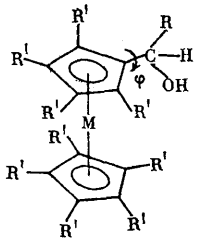
Figure 16. Dependence of the energy of the van der Waals interaction on the pseudo-torsional angle (Mo—S...S—Mo) in the molecules $[C_5R_5Mo(\mu\text{-}S)]_2$ with R = H (*a*) and Me (*b*) and in the molecule $[(C_2H_4S_2)MoS(\mu\text{-}S)]_2$ (*c*); the arrows indicate the values of φ found experimentally in the crystal; *1*, *anti*-isomer; *2*, *syn*-isomer.[116]

last feature led the authors cited to the conclusion that the addition of any group to this cluster through the sp^3 hybridised C atom cannot take place without a change in the structure of the cluster itself.

The same approach was used to study the possibility of variation in the relative arrangement of the parts of the molecules in the dinuclear complexes $[LMoS(\mu\text{-}S)]_2$, where L = $C_2H_4S_2$, C_5H_5, and C_5Me_5.[116] The *syn*- and *anti*-isomers, in which, for a fixed ligand environment of each of the metal atoms, the relative arrangement of these atoms was varied by changing the pseudo-torsional angle Mo—S...S—Mo (φ) (Fig. 15), were examined. The graphs giving the dependence of U_{conf} on φ (Figs. 16*a*—16*c*), including only the non-valence component, show that in the non-crowded molecules with L = $C_2H_4S_2$ and C_5H_5 the angle φ changes over a fairly wide range, which also includes the values of these angles for the corresponding isomers in the crystal. For both of these molecules, the *syn*- and *anti*-isomers have similar energies. The energy difference between these isomers is appreciable only for the complex with the bulkier ligand C_5Me_5. This complex is characterised by narrow ranges of allowed values of the angle φ. At present, only the energetically most favourable *anti*-isomer of this complex has been detected.[116] The slight difference in the energies of the *syn*- and *anti*-isomers (0.59 kcal mol^{-1}), however, does not exclude the existence of the second isomer.

To investigate unusual intramolecular hydrogen bonds, Shubina and co-workers[117–119] undertook a combined spectral, X-ray

diffraction, and calculation study of various carbinol derivatives of metallocenes



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where M = Fe, Ru; R = H, Me, Ph, Mes, etc.; and R' = H, Me. The conformational calculation in this case should have revealed the steric predisposition of these molecules to the formation of H-bonds of different types: OH...M (involving the metal atom) or OH...π (involving the π-electron system of the cyclopentadienyl ligand). Fig. 17 shows several possible orientations of the carbinol group relative to the metallocene ring. From geometric criteria, an O–H...M bond can be formed in case (*A*), an O–H...π bond can be formed in cases (*B*) and (*C*), neither of these bonds is formed in case (*D*).

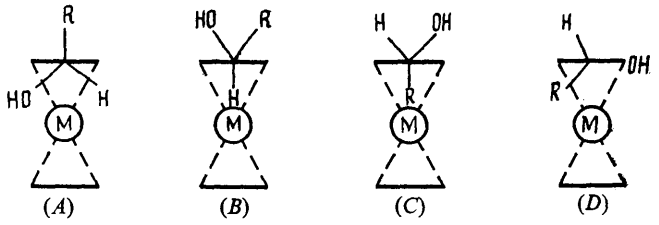


Figure 17. Schematic representation of possible orientations of the carbinol group in metallocenes.

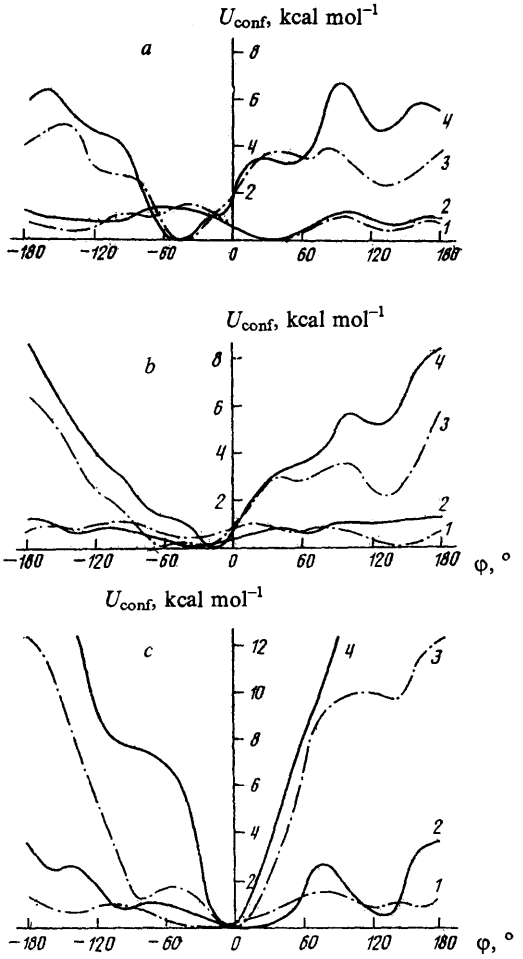
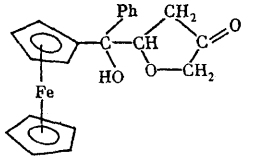


Figure 18. Dependence of the conformational energy of carbinol derivatives of metallocenes on the angle of rotation φ of the carbinol group (M = Fe—continuous line, M = Ru—dot–dash line): *a*, R = Me; *b*, R = Ph; *c*, R = Mes; curves *1* and *2* characterise the molecules with R = H, and curves *3* and *4* the molecules with R = Me.

The dependence of U_{conf} on the angle of rotation φ (C–C–C–O) of the carbinol group has been calculated. The angle φ has negative values for orientation of the OH group towards the metal, and positive values for the arrangement of the OH group above the Cp ring. The calculation showed that for carbinol-substituted metallocenes and nonamethylmetallocenes (M = Fe, Ru) with R = H, there are no ranges of preferential orientation of the OH group. For R = Me, Ph, and Mes (Figs. 18*a*–18*c*), these ranges are distinguished sufficiently clearly only for the nonamethylmetallocene derivatives. For R = Me, the OH group is orientated towards M when M = Fe, and has two orientations when M = Ru; when R = Ph, the OH group is oriented towards the M atom for both metals, but the probability of approach of the OH group to the metal is greater for M = Ru; when R = Mes, the OH group may be turned towards the metal (M = Ru) or may lie in the plane of the Cp ligand (M = Fe), which does not favour the formation of intramolecular H-bonds. In the last case, the calculation shows good agreement with XRD data,[117] according to which the torsional angle φ is 7°.

For the molecule $(C_5Me_5)Fe(C_5Me_4CH(OH)Bu\text{-}t)$ with one bulky substituent on the carbinol group and the molecule



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with two bulky substituents on the carbinol group, the calculation[118] (Fig. 19) indicates that the OH group is oriented towards the metal (negative range of values of the angles φ); this orientation is fairly "rigid" for the first molecule, and less "rigid" for the second. This is in good agreement with the results of a study of the second complex in the crystal[120] (φ = −50.5° from the calculation, and φ = −42.9° from the experiment). The arrangement of the OH group in these molecules makes probable only the formation of the O–H...M bond.

The results of all the calculations are consistent with the infrared spectra of the complexes, which show that they contain O–H...M bonds in those cases where, from steric considerations, only the orientation of the OH group towards the metal is possible, and that two types of bond, O–H...M and O–H...π, are present when there is no steric hindrance.

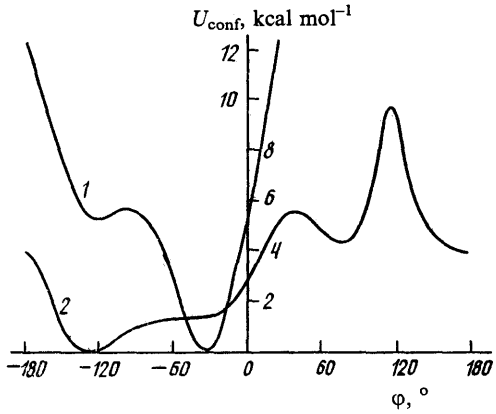


Figure 19. Dependence of the conformational energy on the angle of rotation of the carbinol group φ in the molecules of $(C_5Me_5)Fe[C_5Me_4CH(OH)(Bu\text{-}t)]$ (*1*) and $(C_5H_5)Fe[C_5H_4CPh(OH).(C_4H_5O_2)]$ (*2*).

The orientation of substituents on an asymmetric atom plays an important role in stereoselective reactions. Conformational calculations revealing the role of this factor for organic molecules have been described in detail.[4] Similar calculations were recently carried out[121] for a large number of organometallic complexes containing carbonyl, cyclopentadienyl, phosphine, and acyl ligands on an asymmetric metal atom. The aim of these calculations was to establish the relative orientation of the acyl ligands assuming rigidly fixed coordination (square planar, octahedral, etc.) of the metal atom and a fixed arrangement of the other ligands. The calculations were carried out with allowance for only the energy of the non-valence interaction in the model molecules, which contained the phosphine groups PH_2Ph, and the acyl groups C(O)Me. Fig. 20 shows the Newman projections of complexes of different types, in which the position of the C(O)Me group corresponds to the energy minimum. Complexes ML_4 with square planar, tetrahedral, and pseudo-octahedral (for complexes with Cp ligands) coordination, complexes ML_5 with square-pyramidal and trigonal-bipyramidal coordination, and complexes ML_6 with octahedral coordination were examined.

For all these complexes, the dependence of U_{conf} on the angle of rotation of the C(O)Me group for different filling of the coordination sphere by bulky (PPh_3, Cp) and less bulky (CO) ligands was analysed.[121] The introduction of bulky ligands in most cases does not change the optimum arrangement of the substituents, but it makes the range of allowed orientations narrower, and in some cases decreases the number of such ranges.

The calculation showed a similarity in the orientations of the acyl group in the octahedral and pseudo-octahedral complexes, where one of the faces of the coordination polyhedron is occupied by a Cp ligand replacing three CO groups. The authors cited[121] consider that this similarity [for example in the complexes (4) and (11), and (5) and (12), in Fig. 20] illustrates the so-called isolobal analogy between octahedral and pseudo-octahedral complexes.

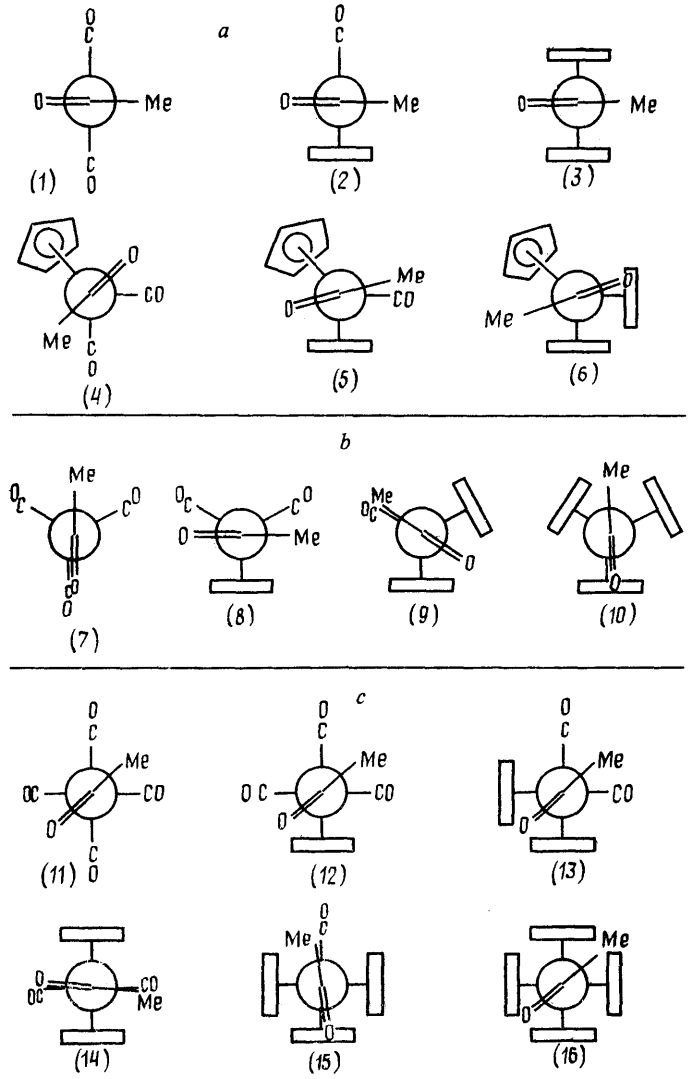


Figure 20. Newman projections of acyl complexes of metals along the line [Me(O)]C–M–CO, corresponding to the minimum energy in complexes ML_4 (*a*), ML_5 (*b*), and ML_6 (*c*); *1–3*, square planar; *4–6*, pseudo-octahedral (tetrahedral); *7–10*, trigonal-bipyramidal; *11–16*, octahedral; the rectangle denotes the ligand PPh_3; in complexes *1–3* and *7–16* the CO group under the plane of the diagram is not shown.

The most interesting and complex conformational calculations for organometallic molecules known at present are the calculations for the molecular complexes of cyclodextrins with ferrocenylacrylic esters

with the 1 : 1 composition, carried out simultaneously by two groups of authors.[122,123] The aim of these calculations was to find the conformation of the clathrate and to establish the mechanism and conformation of the product of the acylation of β-cyclodextrin by ferrocene derivatives (Fig. 21).

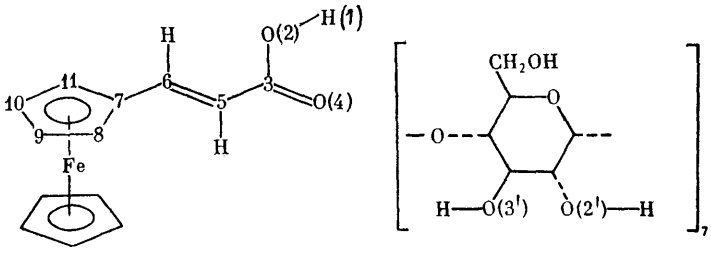


Figure 21. Structure of the molecule of the ferrocenylacrylic ester and the elementary unit of the β-cyclodextrin molecule.

In the first stage of the calculation, the conformations of the isolated molecules forming the complex were determined. It was found, in particular, that the substituent in the ferrocene derivative† has an almost planar structure, and that the *cis*- and *trans*-conformers with respect to the C(3)–C(5) bond have similar energies (with slight preference for the latter). The second stage of the calculation involved the search for the optimum arrangement of the molecule of the ferrocenylacrylic ester in the cavity of the β-cyclodextrin molecule. In this search, in each of the molecules, account was taken of all the components of the conformational energy and the non-valence and electrostatic components of the intermolecular interaction.

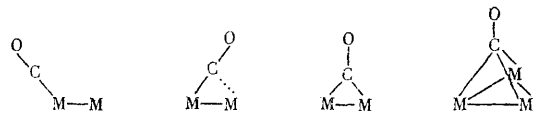
The calculation showed the existence of the three most favourable orientations of the molecule of the ferrocenylacrylic ester in the β-cyclodextrin cavity.[122] In the first of the orientations, the C(3) atom of the ferrocenylacrylic ester approaches the O(2′) atom of β-cyclodextrin, and in the second and third orientations it approaches the O(3′) atom (see Fig. 21). Their relative advantage has the values 0.0, 3.0, and 5.0 kcal mol^{-1} respectively. Calculation of the conformational energy of the acylation products (with allowance for the different arrangements of the parts in the unreacted complex) revealed a slight preference for the product corresponding to the first of these orientations. Evidence in support of the first product is also provided by the fact that the conformation of the acylating agent in this case [acylation at the O(2′) atom] undergoes the smallest change. These conclusions were confirmed by an independent calculation.[123]

2. Metal clusters

The most complex organometallic materials for which the MMM is used at present are cluster molecules. The arrangement of the ligands on the surface of metal clusters, like that round a single M atom, is not rigidly fixed, and may change when the molecule is transferred from the crystal to solution, and in solution the ligands can migrate over the surface of the cluster, that is many clusters are stereochemically non-rigid.[124,125] These features obviously make it difficult to use the ordinary version of the MMM in calculations of the ligand environment of clusters. Earlier, however, it was suggested that the nature of the ligand environment of the metallic nucleus of a cluster is determined by the closest packing of the ligands on its surface.[126] The development of this suggestion has led in recent years to modified versions of the MMM which make it possible to calculate the geometric characteristics of the ligand environment of clusters, using (as in the case of mononuclear complexes) the criterion of the minimum energy of the inter-ligand van der Waals interaction.[127,128]

Thus the authors cited[127,128] developed a model in which the ligands were regarded as points on a sphere approximating the surface of the cluster, between which only the repulsion interaction was specified. The proposed model provides a qualitatively correct description of clusters with CO ligands, but does not reproduce all the details of their structure. It is understandable that the carbonyl ligand can be approximated satisfactorily by a point on a sphere, but this can hardly apply to larger π-bonded hydrocarbon or phosphine ligands, so that the application of this model is restricted considerably.

A more complex version of the MMM, free from the above limitations, has also been developed[125] for carbonyl clusters. The main complication in the description of the ligand environment of the molecules of metal clusters lies in the fact that for the M–L bonds it is difficult to specify the ideal values of the bond lengths and their force constants, since the actual concept of a bond in these molecules is somewhat indefinite. For example, the CO ligand may be terminal, half-bridging, or bridging between two or three metal atoms:



It is considered[125] that in cluster molecules of this type the ligands are joined not to one or several M atoms but to the entire metallic nucleus of the cluster. It is clear that the angle characteristics are also indefinite in this case. Here, therefore, as in mononuclear metal complexes, the non-valence inter-ligand interactions predominate.

The following model has been proposed[123] to take account of these difficulties. All the metal atoms are regarded as spheres with a radius r_m equal to half the length of the M–M bond (usually, in clusters, $r_m \simeq 2.6/2 = 1.3$ Å). Around the centres of the metal atoms, spheres are described with radius r_t equal to the "ideal" (corresponding to the energy minimum) length of the M–C bond with a terminal CO group (1.75 Å). Assuming a definite length r_b for the "ideal" bond M–C with a bridging CO group (in the present case 2.0 Å), the radius of the so-called "trial" sphere r_p (the significance of the notation is clear from Fig. 22) is calculated. As the trial sphere is moved over the surface of the metal core of the cluster, an equipotential surface is constructed from the points of contact; all the points of the surface correspond to a minimum energy of the metal–carbonyl interaction. Examples of these equipotential surfaces for di- and trinuclear clusters are shown in Fig. 23. A similar representation of the surface was adopted for protein molecules[129] in an examination of their solvate layer, from

† The parameters of the potentials for ferrocene derivatives, which make it possible to use the program MM2 for their calculation, have been published.[122,123]

which a mathematical description of this surface was obtained. The movement of a carbonyl ligand arranged at right angles to the equipotential surface is regarded as equally energetically favourable in all directions over the metal cluster.

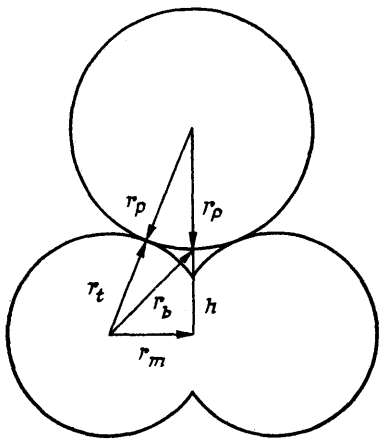


Figure 22. Diagram (section) of the relative arrangement of the metal atoms and the "trial" sphere in a dinuclear cluster.[123]

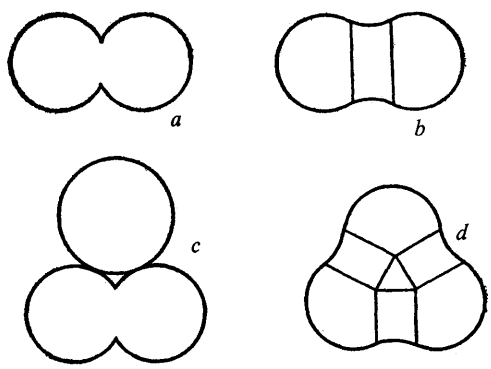


Figure 23. Construction of the equipotential surface of clusters: *a*, metal cores M_2 with intersecting (at a distance r_m) spheres of radius r_t; *b*, the same with a trial sphere of radius r_p touching the fragment M_2; *c*, the equipotential surface of a dinuclear cluster; *d*, the equipotential surface of a trinuclear cluster.[123]

The energies of bond stretching and valence angle deformation are written with allowance for the position of the carbonyl group.

For a terminal CO group, the bond stretching energy is given by

$$E_s = 71.94\, K_s (r - r_t)^2 [1 - 2.0 (r - r_t)],$$

where r is the M–C distance, and K_s the force constant of the bond.

For bridging bonds

$$E_s = 71.94\, K_s (r' - r_p)^2 [1 + 2.0 (r' - r_p)],$$

where r' is the distance from the C atom to the centre of the trial sphere.

The dependence of the energy on the angle of slope of the ligand is given by the expression:

$$E_\theta = 0.021941\, K_\theta (\theta - \theta_0)^2 [1 + 7.0 \cdot 10^{-8} (\theta - \theta_0)^4],$$

where θ is the angle between the C–O bond and the normal to the surface of the cluster, and θ_0 is the ideal value, equal to 0. The angle constant K_θ is small, and the values of the C–M–C angles are determined almost entirely by van der Waals interactions. The geometry of the metal core is not varied in the calculation.

The proposed model[125] was used to carry out calculations for a large number of carbonyl clusters containing from one to four metal atoms. Good agreement between the calculated and experimentally determined coordination was observed for the mononuclear complexes $M(CO)_n$ (n = 4–7). For n = 7, the isomers with coordination of different types (singly-capped octahedron, singly-capped trigonal pyramid, pentagonal bipyramid) have similar energies. In the dinuclear molecules $M_2(CO)_n$ (n = 8, 9), a large number of isomers is detected for the complexes with the less extensively filled coordination layer (n = 8), in agreement with the experimental data. The trinuclear clusters $M_3(CO)_{12}$ are characterised by the existence of three most favourable types of ligand coordination with overall symmetry of the molecules D_{3h}, D_3 (all CO groups terminal), and C_{2v} (two CO groups bridging). For tetranuclear clusters $M_4(CO)_n$ (n = 12–14, 16) with a small number of ligands in the coordination sphere, several versions of the environment corresponding to an energy minimum are possible, whereas increase in the number of ligands usually gives one most favourable type of ligand environment.

The author cited[125] considers that a promising development of the model which he proposed involves the inclusion in it of ligands of different types; this requires the selection of new metal cluster–ligand interaction parameters. The parameters describing the geometry of the organic ligands themselves can be taken, for example, from papers by Allinger and co-workers.[4] The calculation of the ligand environment using this model requires special fairly complex programs.

Mention may be made of another recently published calculation[130] of the geometric characteristics of the molecule of a tetrahedral cluster $M_4(CO)_{14}$ by the usual version of the MMM method with parameters proposed by the authors cited for the interactions including the metal atoms. The calculation was carried out to investigate the influence of steric crowding on the increase in the lengths of the M–M bonds relative to the same bond lengths in the non-crowded molecules. The calculation showed that a definite contribution to the additional elongation of the M–M bonds is made by the C...C non-valence interactions of adjacent CO ligands, but it was not possible to reproduce the values of the M–M bonds characteristic of the cluster $[Fe_3Cr(CO)_{14}][(PPh_3)_2N]_2$, studied by XRD by the same authors.[130]

Brief mention may be made of the possibilities provided by calculations of the conformations of isolated clusters without a ligand environment, which have been described in sufficient detail.[131,132] The atom–atom approximation has for long been used successfully for their description. The calculation of the optimum configuration of clusters of any size, consisting of inert gas atoms, was carried out by minimising the energy of the system using the hard-spheres potential, the Lennard–Jones potential, the Morse potential, etc.[131] The use of long-range potentials gives a significantly smaller number of possible isomers. For small clusters, the number

of isomers with similar energies is fairly large, and decreases with increase in the number of atoms in the aggregate. The same conclusions also apply to metal clusters for which calculations have recently been carried out using special potentials.[133]

The above data, together with the extensive experimental material on the structure of the molecules of metal clusters characterised by different types of arrangement of the metal atoms,[124,134] indicate that the ligand environment may have a significant influence on the metallic core of the cluster. For a complete description of the structure of cluster molecules, it is apparently necessary to develop a model involving the combined calculation of the optimum configuration of the metallic core and the ligand environment with allowance for their constant mutual influence. At the present level of computer technology, this model should be developed in the near future.

V. Summary

The material presented leads to various conclusions about the present possibilities provided by conformation analysis by calculation in the study of organoelemental and organometallic molecules.

It is fairly obvious that for organoelemental molecules in which the coordination of the atom of the element is analogous to that of the carbon atom, the working instrument of conformational analysis by calculation, namely the mechanical model of the molecule, has a sufficiently well developed methodological base (parametrisation and programs). This makes it possible to analyse the conformations of a large number of acyclic, cyclic, and polycyclic organoelemental molecules (mainly organosilicon molecules), and to compare their conformations with those of the corresponding hydrocarbons. It has been found that in spite of the similarity in the coordination of the atoms of carbon and the element, quantitative differences between organic and organoelemental molecules are observed in the values of the barriers to internal rotation and in the ratio of the energies of the conformers, together with qualitative differences in the optimum conformations corresponding to the energy minimum.

The existing level of development of calculation methods for molecules of this class makes it possible to solve for these molecules not only stereochemical problems (the search for the most favourable conformers and the optimum stereo-isomerisation paths) but also the problems of establishing the relative reactivity of molecules and distinguishing the dominant factors (steric or electronic) in chemical transformations. In the near future, the fields of application of the MMM for organoelemental molecules should be as varied as that for organic compounds.

For organometallic molecules and metal clusters, for which conformational calculations have been actively carried out only in the last few years, the situation is different. It has now been shown possible to apply the MMM to molecules of this type, but the parametrisation for mononuclear complexes has not yet been sufficiently developed, and apparently requires improvement. The same applies to the molecules of metal clusters, where in addition to improvement of the parametrisation it is also necessary to continue the search for models making possible the simultaneous description of the arrangement of the atoms in the metallic core and in the ligand environment.

The above results of calculations for organometallic molecules and their comparison with the results of experimental studies for molecules of this type indicate unambiguously the complete qualitative agreement between the results and indicate that the use of the MMM in the stereochemistry of organometallic compounds is promising.

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Carbon dioxide in coordination chemistry and catalysis

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ABSTRACT. All aspects of the fixation of carbon dioxide in the presence of catalytic systems based on transition metals have been reviewed. The results of calculations to determine the nature of the complexes of the CO_2 molecule with transition metal atoms and complexes have been described. The progress made in new fields such as the electrocatalytic, photoelectrocatalytic, photocatalytic, and radiation-catalytic fixation of carbon dioxide has been examined.

The bibliography contains 252 references.

Contents

I.	Introduction	344
II.	Estimation of the stability of the complexes of transition metals with carbon dioxide	344
III.	Complexes of transition metals with carbon dioxide	345
IV.	The insertion of carbon dioxide at an M–X bond	348
V.	Reduction of carbon dioxide	350
VI.	Summary	356

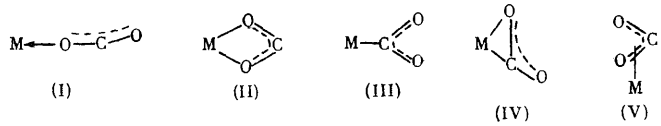
I. Introduction

The problem of the utilisation of carbon dioxide, that is its use as a source of carbon for organic synthesis, is extremely important.[1–8] The solution of this problem is closely related to the solution of the fuel problem (the use of CO_2 to prepare hydrocarbons, methanol, and other compounds), and also to the production of synthetic food. Here it should be borne in mind that carbon dioxide, which is a waste product from various industries, can provide a practically unlimited source of carbon. The fixation of carbon dioxide is of practical interest in connection with the development of waste-free technology and the accumulation of CO_2 in isolated systems such as submarines, spacecraft, etc. The utilisation of carbon dioxide is also of considerable importance for understanding the nature of photosynthetic and chemical synthetic processes. The most important stage in the transformation of carbon dioxide in catalytic processes is the activation of the CO_2 molecule, brought about by its coordination to transition metal compounds acting as catalysts. The most promising method of utilising carbon dioxide involves the use of systems in which the CO_2 molecule can be activated by the combined use of physical (radiation of different kinds, electrolytic reduction, etc.) and catalytic (catalysis by transition metal compounds with cocatalysts of different types) methods. Of particular interest is the fixation of carbon dioxide in aqueous solutions, when water acts as a source of hydrogen; this is related to problems of bioinorganic chemistry.

About 20 years have passed since the publication of the first papers on the preparation of stable complexes of transition metals with carbon dioxide, which have led to the achievements associated with the introduction of this molecule into catalytic processes. In this time, considerable progress has been made in the development of catalytic systems for obtaining organic compounds using carbon dioxide as the source of carbon, and this work has been fairly fully reviewed.[1–8] The present review differs from earlier reviews in its complete coverage of all aspects of CO_2 fixation.

II. Estimation of the stability of the complexes of transition metals with carbon dioxide

As noted in early reviews,[1,2] the coordination of a CO_2 molecule to a transition metal atom (M) can give not only M–O bonds but also M–C bonds. The preparation and determination of the structure of stable complexes of transition metals with CO_2 stimulated the development of methods for calculating the coordination of the CO_2 molecule to metals. In principle, when one CO_2 molecule is coordinated to a metal atom, the following structures may be produced:



(I) (II) (III) (IV) (V)

A virial-statistical method has been used to calculate the stability of structures (I)–(V) for the adducts $M.CO_2$, where M = Cu, Hg, and Tl.[9–14] Adducts of this type have been observed (as ions) in mass-spectrometric studies of the corresponding carboxylates (see the references in the paper by Nekrasov and co-workers[13]). According to the data obtained by mass-spectrometry and calculation, the thallium adducts are the most stable. In the series of structures (I)–(IV), the most stable for all the metals was found to be structure (IV), in which the CO_2 molecule is coordinated through oxygen and carbon atoms simultaneously;[12] the stability of the structures decreases in the order (IV) $\geqslant$ (III) $\gg$ (I) > (II) for copper and (IV) > (III) $\gg$ (I) > (II) for thallium. The results of calculations on these structures made it possible to put forward a mechanism for the fragmentation of copper and thallium carboxylates in the gas phase under the influence of electron impact; the mechanism suggests that the rupture of the C–C bond of the carboxylate gives adducts $M.CO_2$ in which the CO_2 molecule is coordinated to the metal with the formation of a metal–carbon bond.[5,10–12] According to later calculations, the formation of structure (V) is not excluded.[14] In this case, however, difficulties arise, associated with the destabilisation of the adduct as a result of the repulsion of the lone pairs of electrons of the oxygen atoms with the bending of the CO_2 molecule.

It was found by the CNDO-2 method that the stability of the copper adducts $M.CO_2$ decreases in the order (II), (IV) ≫ (III) ≫ (I).[15,16] In the opinion of the authors cited,[15,16] the coordination of a CO_2 molecule to give structure (IV) is favourable because the formation of an M—C bond leads to an increase in the strength of the M—O bond, and vice versa. In the case of titanium (in contrast to copper), the highest stability is shown by the adduct with structure (III), due, in the opinion of the authors cited,[16] to the increase in the separation between the donor levels of the atom of this metal and the unoccupied $2\pi_u$-orbital of the CO_2 molecule on formation of the complex. When there is a high charge on the metal, structure (IV) becomes unfavourable, and coordination of type (I), when the electron density is displaced from the $1\pi_g$-level to an unoccupied *d*-orbital of the metal, is preferred.

The *ab initio* method has been used to determine the nature of the coordination of CO_2 to the metal in the hypothetical complexes $(H_3P)_2Ni(CO_2)$ and $(H_3P)_2Cu(CO_2)^+$.[17] According to the data obtained by the authors cited,[17] who examined only structures of types (I) and (IV), the positively charged copper atom forms structure (I) preferentially, whereas for zerovalent nickel, the formation of structure (IV) is more probable. It is suggested that the coordination of carbon dioxide to nickel to give structure (IV) is brought about by the reverse displacement of electron density from the metal to the ligand, whereas the fact that structure (I) is preferred for copper(I) is due to the strong electrostatic interaction of the metal with the negatively charged oxygen atom. The authors cited do not exclude the possible formation of structure (III) for nickel, if for some reason (the non-availability of a coordination position, etc.) structure (IV) cannot be produced.

Calculation of the stability of the hypothetical complexes $(H_3P)_2Ni(CO_2)$ and $(H_3P)_2Cu(CO_2)^+$ by the extended Hückel method confirmed that structure (IV) is fairly stable for nickel, although its energy advantage over structure (I) is small.[18] The CNDO method was previously used to calculate the stability of the complex $(H_3P)_2Pt(CO_2)$, for which the coordination of CO_2 to the metal to give structure (IV) was found to be most favourable.[19]

The results of a calculation by the CNINDO method indicate that the adduct $Ag.CO_2$, obtained by the co-condensation of the products of the reaction of silver atoms with carbon dioxide, is stable in form (IV).[20] According to data obtained by various authers,[17—20] the CO_2 molecule coordinated to the metal is bent (problems related to the bending of CO_2 on excitation have been examined[1,2]).

Overall, the results of calculations of the stability of the complexes of transition metals with carbon dioxide by different methods indicate that the CO_2 molecule tends to coordinate to a metal atom through oxygen and carbon atoms simultaneously. Coordination to give structure (I) is most probable, however, for a positively charged metal, when the formation of the complex is essentially the result of the first stage of the reaction of the metal of the complex, acting as a Lewis acid, with carbon dioxide. Thus according to a calculation of the stability of the adducts of Zn^{2+} with carbon dioxide, the preferred structure is structure (I) with an equilibrium M—O distance of 1.85 Å.[21] According to calculations and spectral data, the adducts of CO_2 with the alkali metals have structures (I) (C_s) or (II) (C_{2v}) [22,23] (see also the next section).

Structure (I) tends to undergo conversion into structures (III) and (IV) containing an M—C bond, whose formation in existing complexes has been confirmed by X-ray diffraction (see next section). This tendency in turn is the result of the transition from the primary act of activation of the CO_2 molecule in its reaction with the metal atom to give structure (I) to the formation of more stable adducts in which CO_2 is coordinated to the metal not only through an oxygen atom but also through the carbon atom [structures (III) and (IV)].

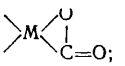
III. Complexes of transition metals with carbon dioxide

1. Stable complexes

Since carbon dioxide is a better acceptor than donor of electron density, it has been suggested that for this molecule, the formation of coordination compounds with the complexes of metals in a low oxidation stable is most characteristic.[2—4] In fact, compounds of this type have now been obtained by the direct action of carbon dioxide on complexes of metals with a low oxidation number, M^0 (Ni, Pt, Rh) or M^+ (Cu, Ag, Rh, Ir). Stable complexes have also been obtained by indirect methods.

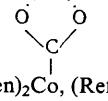
a. Direct method

The direct preparation of complexes of transition metals with CO_2 is of fundamental importance, since it is by this means that the CO_2 molecule can be introduced into catalytic processes. The first stable complex of CO_2 with rhodium(I) was obtained in 1969.[24] Since then, new complexes of various metals have been synthesised, fundamental problems associated with the use of CO_2 as a source of carbon for obtaining organic compounds have been solved, and the principal directions of study in the field of CO_2 fixation have been clearly defined. The number of complexes obtained by the direct method is small, since various side reactions take place. The difficulties associated with the preparation and identification of complexes of metals with CO_2 have been reviewed.[25] X-Ray diffraction has shown that a CO_2 molecule coordinated to a transition metal atom forms an M—C bond:

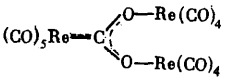


The following complexes have been obtained by the direct method:

$[(C_6H_{11})_3P]_2NiCO_2$ (Ref.26); $(\eta\text{-}C_5H_4Me)_2Nb(CH_2SiMe_3)(\eta^2\text{-}CO_2)$ (Ref.27);

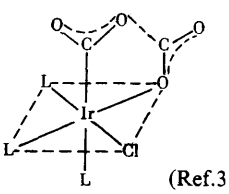


(n-Pr-Salen)$_2$Co, (Ref.28) where Salen = salicylidene-ethylenediamine;



(Ref.29)

$[HOs_3(CO)_{10}CO_2Os_6(CO)_{17}]^-$ (Ref.30);



L = PMe_3

(Ref.31).

A recently prepared complex of rhodium with carbon dioxide is $(diars)_2Rh(\eta^1\text{-}CO_2)Cl$, where diars = $Me_2AsCH_2CH_2AsMe_2$, in which, as shown by X-ray diffraction, the CO_2 molecule is

coordinated to the metal atom only through an oxygen atom, that is to give structure (I) (see previous section).[7] Since X-ray diffraction data are not available, it is impossible to reach an unambiguous conclusion about the mode of coordination of CO_2 in the complex $(dppe)_2RhCl.CO_2$, where dppe = $Ph_2PCH_2CH_2PPh_2$.[32] In the opinion of Areste and Nobile,[33] the action of the phosphines $EtPPh_2$ and $n\text{-}Bu_3P$ on the complex $[Rh(C_2H_4)_2Cl]_2$ and CO_2 gives adducts of two types: $L_3RhCl.CO_2$ and $L_2RhCl.CO_2$. The formation of these adducts was confirmed only by infrared spectroscopy.

According to the same authors,[34] for the nickel complexes $L_2Ni.CO_2$, where L = Et_3P and $n\text{-}Bu_3P$, the bands in the infrared spectrum corresponding to the antisymmetric and symmetric stretches and deformations of the coordinated CO_2 molecule are displaced from 1740 (br., s), 1150 (v.s), 1094 (v.s), 845 (s), and 730 (med) [for $(C_6H_{11})_3P$] to 1660, 1203, 1009, 823, and 750 (for Et_3P) and 1660, 1003, 825, and 750 (for $n\text{-}Bu_3P$).

The reaction of carbon dioxide with the anionic complexes $[(Salen)_2Co]^-$ gives adducts of cobalt with CO_2.[28] From X-ray diffraction data it was concluded that these compounds are complexes of carbon dioxide with cobalt, and that the K^+ cation brings about additional specific coordination of the CO_2 molecule as a result of its reaction with two oxygen atoms of carbon dioxide. Without X-ray diffraction data it is difficult to determine whether the products of the reaction of CO_2 with $NaRe(CO)_5$ or $CpFe(CO)_2MgBr$ are complexes of the metals with carbon dioxide or salts of the metal-carboxylic acids.[34–36] For example, the insertion product obtained by the reaction of CO_2 with $CpFe(CO)_2MgBr$ (an organometallic analogue of the Grignard reagent) is readily alkylated by methyl iodide to give the ester of the iron-carboxylic acid:[35]

$$CpFe(CO)_2MgBr + CO_2 \rightarrow \{CpFe(CO)_2(CO_2MgBr)\} \xrightarrow{MeI} \longrightarrow CpFe(CO)_2CO_2Me.$$

The problems associated with complex formation of this type have been examined in detail[36] (see also the next section). At the present time, because of the lack of X-ray diffraction data, it is difficult to determine the nature of the coordination of the CO_2 molecule in these compounds. Moreover, although in the complexes $[(Salen)_2Co]K$ the insertion of CO_2 is reversible,[28] the insertion of CO_2 into the rhenium and iron complexes[35,36] is irreversible.

The reaction of carbon dioxide with the complex $(dmpe)_2IrCl$, where dmpe = $Me_2PCH_2CH_2PMe_2$, gives the adduct $(dmpe)_2IrCl.CO_2$, which on heating is readily converted into a carboxylate complex of iridium:[37]

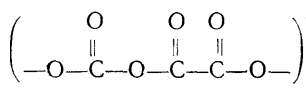
$$(dmpe)_2IrCl \cdot CO_2 \rightleftarrows Me_2PCH_2CH_2P(Me)CH_2CO_2(dmpe)IrCl.$$

If the ligand is not dmpe but diars (diars = $Me_2AsCH_2CH_2.AsMe_2$), the only product is $(diars)_2IrCl.CO_2$, whose infrared spectrum contains bands at 1550 cm^{-1} and 1220 cm^{-1}. The reaction of CO_2 with $(Me_3P)_3IrCl$, however, gives a complex containing two carbon dioxide molecules per metallic centre;[31] one CO_2 molecule is coordinated to the metal through an oxygen atom [structure (I)], and the other through the carbon atom [structure (III)], and the two CO_2 molecules are joined to one another by a C–O bond. It has also been suggested[38] that in the unstable adduct of molybdenum with carbon dioxide $(Me_3P)_3Mo.(CO_2)_2$, the two CO_2 molecules form a similar ring (the infrared spectrum of the adduct of iridium with two CO_2 molecules contains bands at 1725, 1680, 1648, 1605, 1280, 1008, and 790 cm^{-1}). The molybdenum complex readily disproportionates according to the scheme

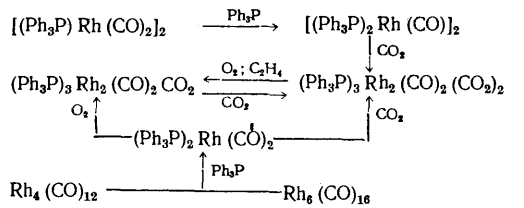
$$2(Me_3P)_3Mo(CO_2)_2 \rightarrow [(Me_3P)_3Mo(CO_3)(CO)]_2,$$

(see also the next section).

The reaction of CO_2 ligands at a metallic centre is an important process for the activation of this molecule, and it determines to a large extent the nature of the final products. The study of the nature of the coordination of several molecules at a metallic centre is of considerable interest for an understanding of the processes involved in the chemisorption of carbon dioxide on the surface of heterogeneous catalysts or on the electrode surface in the electrocatalytic reduction of CO_2. An interesting result is the preparation of an adduct containing three CO_2 molecules per metallic centre, $Mg(CO_2)_3^{2-}$.[39] The adduct was obtained in an inert-gas matrix by the co-condensation of Mg vapour with carbon dioxide. Analysis of the chemical reactions and the infrared spectroscopic data indicates that oxalate and carbonate units are combined in its structure:



The synthesis of the paramagnetic rhodium complex $(Ph_3P)_3Rh_2.(CO)_2(CO_2)_2.C_6H_6$ has been described.[40,41] This complex can be obtained by different methods:



b. Indirect methods

The first complex of a transition metal with CO_2 to be obtained by an indirect method was $(Ph_3P)_3Rh_2(CO)_2.CO_2.C_6H_6$.[42] It was obtained by oxidising a carbonyl group on the metal with oxygen. Reactions of this type have been reviewed.[8] The same complex was synthesised by another method, via an unstable rhodium-carboxylic acid:[41]

$$L_2Rh(CO)OH + CO \rightarrow L_2Rh(CO)CO_2H,$$

$$L_2Rh(CO)CO_2H + L_2Rh(CO)OH \rightarrow L_3Rh_2(CO)_2CO_2 + H_2O + L,$$

$$L = Ph_3P.$$

This complex can be regarded as the rhodium salt of a rhodium-carboxylic acid. The role of metal-carboxylic acids in the preparation of complexes with CO_2 by this method has been examined.[36] In particular, the reaction of a platinum-carboxylic acid with a phosphine complex of zerovalent platinum gives polynuclear complexes with carbon dioxide:[43]

$$2L_2Pt(Cl)CO_2H + L_3Pt \rightarrow [L_2Pt(Cl)CO_2]_2PtL_2 + 2H^+ + L,$$

$$L = Ph_3P.$$

The polynuclear complexes of rhenium[29] and osmium[30] are also probably formed via metal-carboxylic acids. Thus the rhenium complex is formed via the intermediate $(CO)_5ReOH$, which may be present in equilibrium with $(CO)_4ReCO_2H$. In connection with the

preparation of complexes of metals with carbon dioxide via metal-carboxylic acids, mention may be made of the formation of an ester of an iridium-carboxylic acid from a complex with CO_2:[44]

$$dmpe_2\,IrCl\cdot CO_2 + MeSO_3F \rightarrow [dmpe_2Ir(Cl)\,CO_2Me]^+\,SO_3F^-.$$

The existence of the stable rhenium-, iron-, and iridium-carboxylic acids described in the literature extends considerably the possibilities for obtaining transition metal complexes.[36] The use of metal-carboxylic acids is also important because it gives complexes with carbon dioxide in which the M–C bond is fixed on a definite metal.

2. Unstable complexes

The formation of unstable adducts of carbon dioxide with transition metals takes place in the solid, liquid, and gas phases. Thus the co-condensation of silver atoms with CO_2 in a matrix gives the adduct $Ag.CO_2$.[20] From the similarity in the infrared and ultraviolet spectra of this adduct and the corresponding spectra of the complex of nickel with CO_2, whose structure has been determined,[26] it was concluded that the CO_2 molecule is π-coordinated to Ag. Adducts of CO_2 with other metals have been obtained in matrices.[45] It has been suggested that the formation of CO_3 by the ultraviolet irradiation of mercury in a carbon dioxide atmosphere involves the intermediate $Hg.CO_2$.[2] The formation of the adduct $Tl.CO_2$ in the solid phase during the thermal decomposition of thallium(I) carboxylates has been reported.[46]

The formation of unstable adducts $M.CO_2$ in solution has been examined.[1,2] In the formation of the complexes of carbon dioxide with hydride complexes of cobalt and iron, the initial stage of the reaction is the insertion of CO_2 at an M–H bond.[47,48] The existence of the equilibrium

$$(Ph_3P)_3\,Ru\,(H)\,O_2\,CH \rightleftarrows (Ph_3P)_3\,Ru\,(CO_2)\,H_2,$$

and the formation of an intermediate adduct of ruthenium with CO_2 were discussed in a study of the kinetics of the reduction of alkenes by formic acid in the presence of phosphine complexes of ruthenium.[1,8,49] ^1H NMR has been used to study the transformation of ruthenium formates into a complex of ruthenium with carbon dioxide in solution.[50,51] The formation of unstable complexes with CO_2 may take place in the decarboxylation of the fragment $[Ir]O_2CR$,[37] and also copper carboxylates.[52,53] Carbonate and hydrogen carbonate complexes are also formed via unstable intermediates formed by the metals with CO_2 (see next section). The formation of an adduct of cobalt with CO_2 has been noted in the electrolytic reduction of Co^{3+} complexes.[36]

Adducts with CO_2 are formed in the reaction of N-bases with metal-carboxylic acids:[36]

$$[M]\,CO_2H + R_3N \rightleftarrows [M]\,CO_2^- + R_3NH^+.$$

The study of the behaviour of transition metal formates and metal-carboxylic acids in solution is extremely important for an understanding of the mechanism of the preparation of "synthetic gas":[7,36]

$$CO + H_2O \rightleftarrows CO_2 + H_2.$$

Different groups of workers have observed the formation of the following unstable adducts of metals with CO_2 in the gas phase (mass-spectrometric data): $Cu(CO_2)^+$,[54–57] $Cu_2O(CO_2)^+$,[55] $Cu(CO_2)_2^+$,[56] $Cu(O_2CR)(CO_2)^-$,[55] $Cu_2(CO_2)(O_2CR)^+$,[55] $Cu_4(CO_2)_2(CO)^+$,[55] $Cu_4(CO_2)_2(CO)_2^+$,[55] $Cu_4O_2(CO_2)_2^+$,[55] $Re(CO_2)^+$,[58] $(CO)_5Re(CO_2)Re(CO)_4^+$,[29] and $Tl(CO_2)^+$.[11–14,59,60]

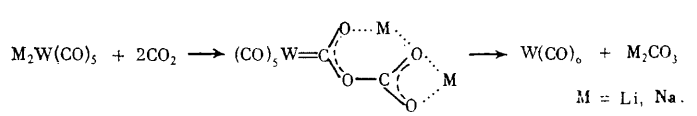
A noteworthy feature is the selective formation of the adduct $Tl.CO_2^+$ from Tl^I carboxylates, which opens up the possibility of studying the mode of coordination of the CO_2 molecule to the metal in the gas phase and its behaviour in chemical reactions.[11–14] The reaction of nickel vapour with CO_2 gives Ni(CO).[61]

3. The formation of carbonate and hydrogen carbonate complexes in the reaction of CO_2 with transition metal compounds

The formation of carbonate and hydrogen carbonate complexes by the reaction of carbon dioxide with transition metal compounds is a side reaction in the preparation of complexes with CO_2, and in most cases takes place under mild conditions.[1,2,26] The formation of the carbonate ion and carbon monoxide can be represented as the result of the reaction of two radical-anions $CO_2^{\cdot-}$ at a metallic centre:[2]

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

Thus the final product of the reaction of $(Me_3P)_4Fe$ with CO_2 is $(Me_3P)_3Fe(CO_3)(CO)$.[62] According to the data obtained,[62] this reaction involves the formation of an intermediate unstable adduct of iron with carbon dioxide. The formation of molybdenum carbonate from an adduct containing two CO_2 molecules per metallic centre was noted in section 1. Carbonates are readily formed by the reaction of CO_2 with hydride complexes of ruthenium, cobalt,[1,26] and rhodium,[26,63] and with alkyl derivatives of cobalt and palladium.[26] In the reaction of CO_2 with anionic complexes of transition metals under mild conditions, disproportionation of carbon dioxide to CO_3^{2-} and CO takes place.[26,64–70] Na_2CO_3 and CO were identified in the reaction of CO_2 with $CpFe(CO)_2Na$.[64] The rate of the reaction of carbon dioxide with anionic complexes of iron, nickel, tungsten, and manganese changes in the same sense as the relative nucleophilic character of the metals. The reaction of CO_2 with the complexes formed by the action of organic derivatives of Li, Mg, and Al on the hydrides $CpMH_2$, where M = Mo or W, has been studied.[65–67] The formation of the carbonate ion and CO involves the insertion of CO_2 at the M–Li, M–Mg, or M–Al bonds respectively. It has been suggested that in the reaction of the tungsten dianion with CO_2, an adduct with two CO_2 molecules is formed as an intermediate:[70]



The unstable adduct $[Ir]CO_2[Al]$ is probably liberated in the hydrolysis of an ester of an iridium-carboxylic acid in the presence of $AlCl_3$.[71]

The CO_2 molecule, which is a heterocumulene, contains nucleophilic and electrophilic centres, so that it can be activated extremely effectively by coordination to metals with different electron-donor and electron-acceptor properties (bifunctional catalysis). Catalysis of this type reveals most clearly the role of the catalytic centre containing the transition metal, to which carbon dioxide is able to coordinate to give an M–C bond, and also the role of metals of groups I–III, capable of forming M–O bonds (see next section).

IV. The insertion of carbon dioxide at an M–X bond

1. The insertion of carbon dioxide at an M–H bond

The problems associated with the insertion of a CO_2 molecule at an M–H bond have been reviewed in detail.[1,7,47,48] The insertion can take place in two ways:[1,7]

$$[M]-H + CO_2 \begin{cases} \longrightarrow [M]O_2CH \\ \longrightarrow [M]CO_2H \end{cases}.$$

The insertion products may be formed at an intermediate stage in the reduction of carbon dioxide to HCO_2H, etc. For example, the reaction of carbon dioxide with $(Ph_3P)_2Cu.BH_4$ [72] or with $(dppe)ReH_3$ [73] gives $L_2Cu(\eta^2\text{-}O_2CH)$ and $(dppe)ReO_2CH$ respectively. The reaction of the cluster $(Ph_3PCuH)_6$ with CO_2 has been studied.[74] The main product is formate, but the authors cited suggest that an unstable copper-carboxylic acid is formed in one of the stages. Carbon dioxide can be selectively reduced to MeO^- by treatment with the hydride complex of zirconium $Cp_2Zr(H)Cl$.[75] In the $TiCl_4-Mg-CO_2-THF$ system, the formate complex $Ti(O_2CH)_2.MgCl_{1.5}.THF$ is formed.[76] The source of hydrogen (moisture or the solvent) is not indicated, but it is stated that in the reaction of $TiCl_4$ with Mg in THF it is possible to isolate a complex which gives titanium formate when treated with CO_2:

$$2TiCl_4.2THF + 6Mg + 2THF \xrightarrow{Ar} (TiMg_2Cl_2.THF)_2 + 2MgCl_2.THF \xrightarrow{CO_2} Ti(O_2CH)_2MgCl_{1.5}.THF.$$

The presence of traces of moisture in the solvent or the addition of water may have a significant influence on the nature of the catalytic processes involving carbon dioxide.[1,7,8] Thus the reduction of CO_2 by molecular hydrogen in $C_6H_6-H_2O$ solution in the presence of basic additives and phosphine complexes of palladium, rhodium, ruthenium, and iridium gives formic acid.[77] A significant feature is that when these systems contain hydrogen carbonate, HCO_2H is also formed in the absence of CO_2. In this connection it should be noted that transition metal compounds are able to activate water with the formation of hydride complexes. In the presence of phosphine complexes of palladium and copper as catalysts, and of alcohols and amines as additives, methane is formed in addition to derivatives of formic and oxalic acids.[78] The formation of CH_4 from CO_2 and H_2 has also been observed in the presence of ruthenium compounds deposited on an Al_2O_3 surface.[79]

A phosphine complex of ruthenium or its hydride cluster have been used for the hydrosilylation of carbon dioxide.[80,81] This reaction takes place with the intermediate formation of ruthenium formates.

2. The insertion of carbon dioxide at an M–C bond

The solution of the fundamental problems associated with the insertion of CO_2 at a transition metal–carbon bond[1] stimulated the appearance of a large number of publications on this topic. From the wide range of studies it is necessary to distinguish those involving the investigation of the mechanism of the reactions leading to the formation of the M–C bond and the preparation of organic products by the carboxylation of intermediates produced, for example, by the oligomerisation or polymerisation of unsaturated compounds in the presence of catalysts. Of particular importance is the formation of organic products as a result of the carboxylation, by carbon dioxide, of organometallic compounds produced by the activation of C–H bonds by transition metal complexes. Thus acetonitrile, acrylonitrile, and phenylacetylene are carboxylated in the presence of phosphine complexes of rhodium and iridium ML_4^+, where L = a trialkyl- or triarylphosphine:[82]

$$L_4M^+ + RH \rightleftarrows L_4M(R)H \underset{-CO_2}{\overset{+CO_2}{\rightleftharpoons}} L_4M(O_2CR)(H).$$

It has also been shown that it is possible in principle to carry out the carboxylation of cyclohexene in the presence of H_2 and of amines to the corresponding acid amides on complexes of iridium, rhodium, platinum , and palladium.[83]

Since the insertion of CO_2 at an M–C bond has been fairly fully reviewed,[1,3,5,7] only the principal results obtained in the last ten years will be presented here.

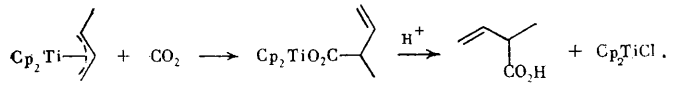
Elements of group I (copper, silver). The insertion of CO_2 at an M–C bond in the copper complex $(Ph_3P)_2CuMe$ and the organometallic derivatives of silver RAg, where R = n-tolyl, etc., gives in the first case the compound $(Ph_3P)_2CuO_2CMe.CO_2$, and in the second case the silver complexes $RAgCO_2Ag$, which can be regarded as the silver salts of silver-carboxylic acids.[1] The reversible insertion of CO_2 at a Cu–C bond has been studied in detail (see the review of Kolomnikov and Grigoryan[1] and section III.2 of the present review).

The reaction of carbon dioxide with the compounds RM, where R = fluorenyl or phenylacetylenyl, and M = Cu or Ag, in the presence of different ligands (BuNC, R_3P, Py, etc.) in a number of cases gives the corresponding acids, identified as the esters.[84] Carbon dioxide can be inserted at the M–C bond in the compound $(CF_3)_2CFAg$, to give the corresponding carboxylate.[92] It has been reported that CO_2 is not inserted at the M–C bond in the complex Ph_3PAuMe, even under severe conditions.[1]

Elements of group II (zinc). The insertion of carbon dioxide at the zinc–carbon bond in the compounds ZnR_2, where R = Alk, has been reported in connection with the use of organometallic compounds of zinc as catalysts of the co-condensation of oxiranes with CO_2.[1,85]

Elements of group IV (titanium, zirconium). The titanium and zirconium compounds R_4M, where R = CH_2Ph, react readily with carbon dioxide to form unstable carboxylates.[1] The reaction of CO_2 with diphenyltitanocene to give the cyclic carboxylate $Cp_2TiO_2CC_6H_4$ has been studied in detail.[1] The mechanism of the thermal decomposition of the compounds Cp_2TiR_2, where R = *m*- or *p*-tolyl, in a carbon dioxide atmosphere has been studied.[86] The detection, among the products of this reaction, of the cyclic titanium carboxylates $Cp_2TiO_2C[m(p)\text{-}C_6H_4Me]$, similar to that noted above, made it possible to determine the nature of the reaction taking place and to establish fairly reliably the appearance of a dehydrobenzene intermediate of titanium in this reaction.

The reaction of carbon dioxide with the organometallic compounds of titanium(III) Cp_2TiR, where R = allyl or methallyl, has been studied.[87–90] The insertion of CO_2 at the M–C bond gives the corresponding carboxylates Cp_2TiO_2CR. In the case of the alkylallyl ligand, asymmetric insertion takes place:[90]

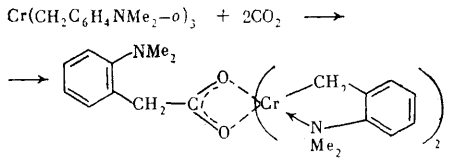


The zirconium compounds $Cp_2Zr(R)Cl$, where R = Me or C_6H_{11}, do not react with carbon dioxide.[83] The reaction of Ph_2ZrEt_2O with CO_2, however, readily gives a zirconium carboxylate.

Elements of group V (vanadium). The reaction of the vanadium(III) compounds R_3V, where R = C_6H_5 or CH_2SiMe_3, with CO_2 gives vanadium(II) carboxylates:[91]

$$2R_3V.THF + CO_2 \rightarrow V(O_2CR)_2 + R_4V.THF.$$

Elements of group VI (chromium, molybdenum, tungsten). Carbon dioxide is not inserted at an M–C bond of the complex $(PhCH_2)_3Cr.H_2O$,[1] but this reaction can take place with the complex $Cr(CH_2C_6H_4NMe_2\text{-}o)_3$:[92]



The reaction of CO_2 with $MeCr(CO)_5^-$ anions has been reported.[7,93] The rate of formation of the carboxylates $MeCO_2Cr(CO)_5^-$ increases considerably when alkali metal salts are added. A similar reaction takes place with $MeW(CO)_5^-$.[94]

Carboxylates are also formed in the reaction of carbon dioxide with bis(ethylene)-complexes of molybdenum and tungsten:[95]

$$trans\text{-}[M(C_2H_4)_2(PMe_3)_4] \xrightarrow{CO_2} \tfrac{1}{2}[M(H_2CCHCO_2H)(C_2H_4)(PMe_3)_2]_2.$$

The reaction of $CpW(CO)_3Me$ with carbon dioxide gives the corresponding carboxylate.[96] The rate of this reaction is increased when Lewis acids are added.

The addition of transition metal salts to the $C_6H_6-AlX_3-CO_2$ system increases the yield of benzoic acid.[97] The highest yield was observed when $MoCl_5$ was added, and this may be due to the formation of an intermediate containing an Mo–C bond.

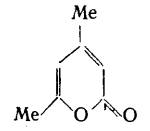
Elements of group VII (manganese). Carbon dioxide reacts readily with $(PhCH_2)_2Mn$ to give an unstable carboxylate.[98]

Elements of group VIII. The reversible insertion of CO_2 at the Fe–C bond formed by the rupture of the P–C bond in the complex $(Me_3P)_4Fe$ has been noted.[62] The intermediate formed in the reaction of a phosphine complex of iron with acetonitrile reacts with CO_2 to give cyanoacetic acid:[99]

$$(dmpe)_2Fe(H)(CH_2CN) \xrightarrow{CO_2;\ H^+} NCCH_2CO_2H.$$

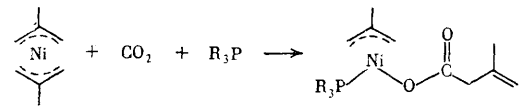
For organometallic derivatives of cobalt it has been shown that, in addition to the usual insertion of carbon dioxide at a Co–C bond to give a carboxylate, "anomalous" insertion to give the ester of a cobalt-carboxylic acid is possible.[1,7] Carbon dioxide can be inserted at the Co–Me bond of a complex of cobalt with salicylidene-ethylenediamine.[1] This reaction is promoted by the addition of dithiols, and does not take place in their absence.

The reaction of carbon dioxide with the rhodium complexes $(Ph_3P)_3RhR$, where R = Me or Ph, gives the carboxylates $(Ph_3P)_3RhO_2CR$.[1] In the oligomerisation of methylacetylene in the presence of *cis*-$(dppe)Rh(CO)_2^+$, 4,6-dimethyl-2-pyrone is formed as the product of the oligomerisation of the alkene and the insertion of CO_2 at a rhodium–carbon bond:[100]

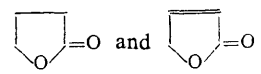


The CO_2 molecule undergoes reversible insertion at an Ir–C bond with the rupture of a P–C bond formed by the phosphine ligand in the complex $(dmpe)_2IrCl$.[37] The insertion of CO_2 at Ir–C and Rh–C bonds has been discussed.[82]

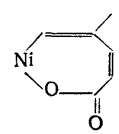
Carbon dioxide is readily inserted at an Ni–C bond in its reaction with bis(methylallyl)nickel in the presence of phosphines:[101]



The author cited also described the formation of cyclic derivatives of nickel as the products of the cyclodimerisation of butadiene on a nickel complex and the insertion of CO_2 at an Ni–C bond. The reaction of CO_2 with bis(allyl)nickel in dimethylformamide gives lactones:[102]

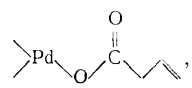


The reactions of carbon dioxide with intermediates formed in the oligomerisation of hex-1-yne and but-2-yne in the presence of phosphine complexes of zerovalent nickel have been studied.[103,104] The final products are substituted pyrones,[103] and a complex of the following type[104]

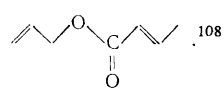


is formed in the reaction. The insertion of a CO_2 molecule at an Ni–C bond has also been described by Yamamoto and Yamamoto.[105]

A wide range of reactions involving the insertion of CO_2 at a Pd–C bond are now known. The telomerisation of butadiene in a CO_2 atmosphere readily gives lactones and octadienyl esters.[106,107] An interesting feature is that the rate of the dimerisation of butadiene and isoprene is increased in the presence of carbon dioxide. The action of carbon dioxide on bis(η^1,η^3-allyl)Pd.R_3P gives the fragment

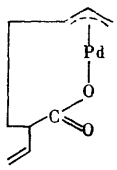


which subsequently reacts with carbon monoxide to give


[108]

The similar insertion of CO_2 at a Pd–C(η-allyl) bond has been reported.[109] In the carboxylation of bis(η^3-butenyl)palladium, but-1-ene-3-carboxylic acid is formed selectively after acidification.[110]

This reaction takes place with the formation of the intermediate



In a CO_2 atmosphere in the presence of the catalytic system bis(allyl)Pd$-PR_3$, allene undergoes copolymerisation to give a mixture of esters and lactones.[111] The corresponding lactone is formed smoothly from methylcyclopropane and CO_2 in the presence of $(dppe)_2Pd$.[112] The reversible insertion of carbon dioxide at a Pd$-$C bond to give cyclic adducts has been observed.[113]

Finally, carbon dioxide can also be inserted at an M$-$C bond in reactions involving lanthanides and actinides.[114,115]

3. The insertion of carbon dioxide at M$-$O and M$-$N bonds

The insertion of CO_2 at an M$-$OH bond can give a stable hydrogen carbonate complex or an unstable adduct with carbon dioxide:[1,2]

$$[M]{-}OH + CO_2 \rightleftarrows [M](CO_2)OH \rightarrow [M]O_2COH.$$

In the absence of X-ray diffraction data, the determination of the nature of the complexes formed is extremely difficult.[25] The ease of formation of hydroxo-complexes of transition metals in catalytic systems in the presence of traces of water makes it possible to regard this reaction in the case of reversible addition as a stage in the activation of the CO_2 molecule.

Copper(I) alkoxides readily undergo the following reversible reaction:[25]

$$CuOR + CO_2 \rightleftarrows CuO_2COR.$$

Zinc-containing complexes and enzymes such as carbanhydrase, containing a Zn$-$OH bond, can catalyse the reaction of CO_2 and H_2O to give carbonic acid.[1] The ready formation of hydrogen carbonates and alkyl carbonates has also been observed in reactions involving hydroxo-complexes and alkoxides of ruthenium, rhodium, iridium, palladium, etc.[25]

The insertion of CO_2 at an M$-$N bond is similar to its insertion at an M$-$O bond. The addition of carbon dioxide again may be reversible, or may give stable carbamates. The structure of various carbamates obtained in this way has been established by X-ray diffraction.[2] The insertion of a CO_2 molecule at an M$-$N bond has been studied in detail (see for example the papers of Chisholm and co-workers,[116,117] and references therein). The formation of carbamates by the insertion of CO_2 at an M$-$N bond has been observed for compounds of titanium,[118] tungsten,[2,119] and uranium.[120]

The insertion of CO_2 at a Cu$-$N bond is reversible.[121] EPR has shown unambiguously that the reaction of copper(II) ephedrinate with carbon dioxide gives an unstable carbamate,[122,123] and not a complex of copper with CO_2, as suggested in early studies.

Finally, it may be noted that the insertion of CO_2 at M$-$O and M$-$N bonds, like its insertion at an M$-$C bond, provides a new method for obtaining the hydrogen carbonates, carbamates, and carboxylates of transition metals, lanthanides, and actinides. It is well known that the addition of amines to catalytic systems facilitates the insertion of carbon dioxide at an M$-$C bond, that is the activation of the latter.[1] It is also possible that carbon dioxide is activated in these systems as a result of simultaneous reaction with the atoms of the transition metal and nitrogen (bifunctional catalysis). This indicates the importance of the study of the mechanism of the insertion of carbon dioxide at an M$-$N bond for the solution of the problem of involving this molecule in catalytic processes to give organic products.

V. Reduction of carbon dioxide

1. Chemical reduction of carbon dioxide

The reduction of carbon dioxide by alkali metal amalgams gives oxalate ion in the absence of moisture, and formic acid in the presence of moisture.[2] In addition to oxalic acid, the products of the reaction of CO_2 with alkali metal amalgams in aprotic media, after hydrolysis, contain acetic, malonic, glycollic, tartaric, and other acids.[2]

The coordination of CO_2 to the alkali metals, and the reaction products, have been studied.[22,23] An interesting feature is that the adduct $LiCO_2CO_2$ was detected among the products of the reaction of CO_2 with lithium vapour in a matrix. The published[22] reaction scheme explains, on the one hand, the formation of the oxalate ion, and on the other hand the formation of the carbonate ion and carbon monoxide.

An example of bifunctional catalysis is provided by the reduction of carbon dioxide in the presence of the Cp_2TiCl + Al system in tetrahydrofuran.[124] $Cp_2Ti(CO)_2$ is formed in this system as the main product, in 80% yield. The influence of the Lewis acids VCl_4, $HgCl_2$, and $GaCl_3$ on the yield of dicarbonyltitanocene has been studied. The carbonate $(Cp_2Ti)_2CO_3$ was detected in addition to the titanium carbonyl.

The reduction of carbon dioxide by molecular hydrogen to methanol and methane in the presence of bifunctional catalysts has been examined.[125]

The reduction of CO_2 in aqueous media, when the water molecules act as hydrogen donors, are of particular interest. An extremely important feature of these systems is the ability of the transition metal to activate a water molecule with the formation of a hydride complex. Thus the splitting of water by cobalt complexes takes place under mild conditions according to the scheme[126]

$$2[Co] + H_2O \rightarrow [Co]H + [Co]OH,$$

and its splitting by phosphine complexes of platinum takes place according to the scheme[127]

$$[Pt] + H_2O \rightarrow H[Pt]OH.$$

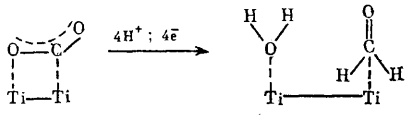
The hydrogenating power of the cobalt complex increases when reducing agents (Zn/Hg etc.) are introduced into the system.[126]

In the reduction of salts and oxides of vanadium by amalgamated zinc in aqueous solutions in a CO_2 atmosphere, the chief reaction product is HCO_2H, whereas malic acid is formed preferentially under the same conditions in the presence of molybdenum derivatives, and malic and tartaric acids in the presence of $TiCl_4$.[128] In aqueous solutions in the presence of the $Ti(SO_4)_2-Al/Hg$ system, formaldehyde and formic acid are produced (10% of the yield of H_2CO).[129] HCO_2H, H_2CO, MeOH, and CH_4 have been detected in the reduction of carbon dioxide in acidic solutions in the presence of sodium amalgam and compounds of manganese, tungsten, and molybdenum. The main product is methanol in the absence of oxygen, and H_2CO and MeOH in the presence of oxygen.

In the presence of the $Ti^{2+}-Al/Hg$ system at pH 1.7 and a CO_2 pressure of 5 atm, the main product of the reduction of CO_2 is H_2CO, whereas in the $Cr^{3+}-Al/Hg$ system, HCO_2H is formed preferentially. The selective reduction of carbon dioxide to formaldehyde in aqueous solution was observed in the presence of the $TiCl_3-Al/Hg$ system.[130] The competing reaction of molecular hydrogen liberation takes place in parallel. The highest yield of H_2CO is achieved at pH 3.5. An interesting feature is that at pH 3.8 in aqueous solutions, the following equilibrium is established[2]

$$CO_2^{\cdot-} + H^+ \rightleftarrows \dot{C}O_2H.$$

It has been shown using $^{14}CO_2$ that the reduction of CO_2 in the presence of the $Ti^{3+}-Al/Hg$ system is a four-electron process taking place according to the scheme



2. The electrochemical and electrocatalytic reduction of CO_2

a. Electrochemical reduction

Considerable attention has been paid to the electrolytic reduction of carbon dioxide in aprotic and proton-containing electrolytes.[2,131-136] The interest in this problem is due largely to the utilisation of CO_2 in isolated systems,[135] and also in relation to the production of organic compounds of interest as future sources of energy (HCO_2H), MeOH, CH_4, etc.) or as foodstuffs.[136-138]

The principal reactions in the electrolytic reduction of carbon dioxide are the formation of oxalate or carbonate ions and carbon monoxide in aprotic media, and the formation of formic acid in aqueous media and in general in the presence of proton donors.[2,131-134] In all cases, the radical-anion $CO_2^{\cdot-}$ is formed in the first stage as the product of electron transfer from the electrode surface to an adsorbed CO_2 molecule:

$$CO_2 + e^- \rightarrow CO_2^{\cdot-} \begin{cases} \xrightarrow{+(CO_2)} CO_3^{2-} + CO \\ \xrightarrow{+(CO_2^{\cdot-})} C_2O_4^{2-} \\ \xrightarrow{+H^+(+e^-)} HCO_2^- \end{cases}$$

The formation of the radical-anion $CO_2^{\cdot-}$ requires a fairly high potential. Thus according to Eggins and McNeill,[139] the direct reduction of carbon dioxide takes place with great difficulty at a potential of -2.0 V (normal hydrogen electrode). In aqueous solutions, this high potential lowers the yield of organic products as a consequence of the competing process of molecular hydrogen liberation.

In a study of the mechanism of oxalate formation, two radical species were detected in the reaction mixture:[134,140]

$$CO_2 + e^- \rightarrow CO_2^{\cdot-},$$
$$CO_2^{\cdot-} + CO_2 \rightarrow CO_2CO_2^{\cdot-},$$
$$(CO_2)_2^{\cdot-} + e^- \rightarrow C_2O_4^{2-}.$$

According to Kafafi and co-workers,[141] the oxalate ion is formed by the dimerisation of two $CO_2^{\cdot-}$ radical-ions. An interesting feature is that the formation of dimers $M(CO_2CO_2)^-$ was suggested as one of the stages in the reaction of alkali metal vapour with CO_2 [141,142] or in the insertion of this molecule at an Fe–Na bond[64] (see also section III). When the adsorption of the dimer $CO_2CO_2^{\cdot-}$ on the electrode is weak, the oxalate ion is formed, and when its adsorption is strong, the carbonate ion and CO are formed.[143] On Pt, Au, and Ag electrodes in DMSO and other aprotic solvents, carbon monoxide is formed,[144-146] whereas on Hg and Pb electrodes in DMF and DMSO, $C_2O_4^{2-}$ is liberated in addition to CO.[131] The lead electrode is preferred for the preparation of oxalate, and the mercury electrode for the preparation of CO. On In, Sn, and Zn electrodes in DMSO at an increased CO_2 pressure, the main product is carbon monoxide.[147] A systematic study of the influence of the electrode material, the carbon dioxide pressure, and other parameters on the yield of oxalic acid in aprotic solvents has been carried out.[139,148] The cathode materials studied were Pb, Pb/Hg, stainless steel, Cr, Cd, Al, Cu, Zn,[139] glass carbon, Hg, Pt, Pb, and Au.[148]

In aprotic media, other organic products are formed in addition to oxalate and carbonate ions and carbon monoxide. Thus at a lead cathode in DMSO, in addition to oxalate, another ten products were detected, including propionic, maleic, tartaric, and other acids.[147] The formation of various organic products in the synthesis of oxalic acid in aprotic solvents has been reported.[131,150] In the presence of moisture in an aprotic solvent, hydroxyacids are formed in addition to oxalate and HCO_2H.[2,147,149] Thus in the presence of water, glycollic acid is liberated at a Pb electrode,[131,151] and malic acid at an Hg electrode.[152]

As noted above, in aqueous solutions the main product of the reduction of carbon dioxide is formic acid. HCO_2H is formed via the radical-anion $CO_2^{\cdot-}$. The electrolytic reduction can take place by a one-electron or by a two-electron mechanism:[2,133]

$$CO_2 + e^- \rightarrow CO_2^{\cdot-},$$
$$CO_2^{\cdot-}(ads) + H_2O \rightarrow CO_2^{\cdot-}(H_2O),$$
$$2\,CO_2^{\cdot-}(H_2O) \rightarrow CO_2 + HCO_2^- + OH^-,$$

or

$$CO_2 + e^- \rightarrow CO_2^{\cdot-}(ads),$$
$$CO_2^{\cdot-}(ads) + e^- \xrightarrow{H_2O} HCO_2^- + OH^-.$$

A mechanism for the electrolytic reduction of carbon dioxide with the simultaneous transfer of two electrons in the CO_2 molecule has been proposed:[153]

$$CO_2 + 2e^- \rightarrow CO_2^{2-},$$
$$CO_2^{2-} + H_2O \rightarrow HCO_2^- + OH^-.$$

The formation of CO_2^{2-} in the reaction of carbon dioxide with alkali metals has been reported.[154] The CO_2 pressure has a significant influence on the order of the reaction.[155]

The $CO_2^{\cdot-}$ radical-anion is extremely unstable, making it difficult to study the mechanism of the electrolytic reduction of carbon dioxide by the methods of electrochemical kinetics.[131] From known thermodynamic quantities, the electron affinity of CO_2 in aqueous solution has been estimated as ~ 0.5 eV.[155,156] The highest current efficiency under optimum conditions was observed at -1.9 V (silver chloride reference electrode) at Zn, Pb, and In cathodes, and at -1.7 V at an Sn electrode.[157] The study of cathode materials with medium and high hydrogen overvoltages showed that in the electrolytic reduction of carbon dioxide, the overvoltage increases in the order Sn < Cu < Zn < Cd < Pb < Au [158] (see also the paper by Vasil'ev and co-workers[133]). The highest efficiency in this process is shown by metals with a medium overvoltage. The high overvoltage at the Sn electrode also ensures high rates of the

electrolytic reduction of CO_2.[159] In the electrolytic reduction of carbon dioxide in aqueous solutions, the formation of propionic[160] and butyric[161] acids in addition to HCO_2H has been noted.

The more extensive reduction of carbon dioxide to formaldehyde, methanol, and methane is accompanied by the transfer of four, six, and eight electrons respectively, that is it requires a much greater expenditure of energy:[162]

$$CO_2(gas) + 2H_2O(liquid) = HCO_2H(solv.) + \tfrac{1}{2}O_2 \quad (E^0 = 1.428 \text{ eV});$$

$$CO_2(gas) + H_2O(liquid) = H_2CO(solv.) + O_2(gas) \quad (E^0 = 1.350 \text{ eV});$$

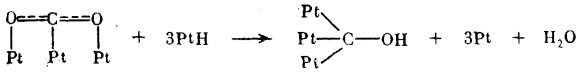
$$CO_2(gas) + 2H_2O(liquid) = MeOH(solv.) + \tfrac{1}{2}O_2 \quad (E^0 = 1.119 \text{ eV});$$

$$CO_2(gas) + 2H_2O(liquid) = CH_4(gas) + 2O_2(gas) \quad (E^0 = 1.037 \text{ eV}).$$

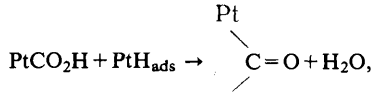
Cyclic voltammetry, preparative electrolysis, and other methods have been used to make a detailed study of the mechanism of the electrolytic reduction of CO_2 to H_2CO and HCO_2H at Hg, Pb, and Sn electrodes in the pH range 6.8–13.0.[137]

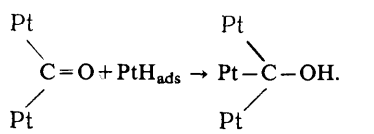
At a platinum electrode in a saturated carbonate solution in a cell with non-separated anode and cathode compartments, formaldehyde is formed in addition to HCO_2^-.[163,164] Fairly high methanol current efficiencies are achieved in the electrolytic reduction of carbon dioxide at an In cathode in lithium carbonate solution.[136] HCO_2H is reduced in acidic media at Pb and Sn to methanol.[137] At a dropping mercury electrode, the reduction of H_2CO to MeOH takes place by two different mechanisms, depending on the pH of the medium. The more extensive reduction of HCO_2H on Sn at comparatively low current densities, in the opinion of the authors cited,[137] is due to the formation of organotin compounds on the electrode surface. The formation of hydrocarbons in the electrochemical reduction of carbon dioxide at an Ag electrode has been reported.[165] In the opinion of the authors cited, the electrolytic reduction of CO_2 passes through a stage involving the formation of unstable silver formate on the electrode surface.

The mechanism of the chemisorption of carbon dioxide in its electrolytic reduction at smooth electrodes is of fundamental importance.[134,166,167] This problem is closely related to the chemisorption of carbon dioxide on the surface of heterogeneous catalysts,[2] and also to the coordination of CO_2 to metals in matrices or in various metallic centres. Of particular interest in this connection is the coordination of carbon dioxide to the surface of a platinum electrode through the carbon atom with the subsequent formation of organometallic adducts during the reduction:[166]



$$Pt_3(CO_2)_{ads} + PtH_{ads} \rightarrow Pt{-}CO_2H,$$





As already noted in section III, X-ray diffraction data show that the bent CO_2 molecule forms a complex with three metal atoms (rhenium and osmium). It is quite possible that a CO_2 molecule coordinated on the surface of a platinum electrode forms a π-allyl adduct. In this connection it should be noted that in the chemistry of coordination compounds there are known cases of the transfer of an allyl ligand from one metallic centre to another.[168,169] Transfer of this kind is particularly important in the electrocatalytic reduction of carbon dioxide.

Hydrogen chemisorbed on a Pt electrode can reduce carbon dioxide to formic acid.[170] The reaction of CO_2 with H_{ads} at the surface of a platinum electrode in 0.5 M sulphuric acid gives the fragment $[Pt]CO_2H$.[171] As noted in section III, the action of water on a cationic complex of platinum gives a stable platinum-carboxylic acid $(Et_3P)_2Pt(Cl)CO_2H$.[36] The formation of esters of a platinum-carboxylic acid of the type $[Pt]-CO_2R$ was detected in the electrocatalytic carboxylation of unsaturated compounds in the presence of platinum clusters.[172] To this it should be added that carbon dioxide can react with the hydride complexes of transition metals in two ways:[1,2,173]

$$[M]{-}H + CO_2 \rightarrow [M]O_2CH,$$
$$[M]{-}H + CO_2 \rightarrow [M]CO_2H,$$

that is with the formation of either formates or metal-carboxylic acids.

Fundamental difficulties in the electrolytic reduction of CO_2 at smooth electrodes are associated with increasing the current density. The low current density is a consequence of the low solubility of carbon dioxide in many solvents. This problem can be solved, in particular, by using porous electrodes, increasing the CO_2 pressure, introducing catalytic additives, etc.

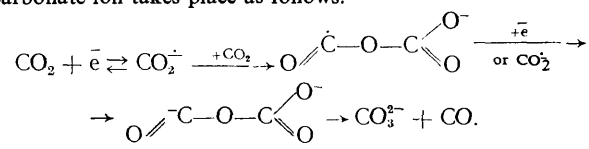
b. Electrocatalytic reduction

In the last ten years, a fairly large number of published papers have described the electrolytic reduction of carbon dioxide in the presence of transition metal compounds acting as catalysts. The introduction of transition metal compounds into the electrocatalytic circuit makes it possible to solve a number of fundamental problems, in particular to lower considerably the potential of the electrolytic reduction of CO_2, to create conditions for many-electron transfer, etc. The nature of the transition metals whose compounds are used as catalysts determines the specific features of the electrocatalytic stage and hence the organic reaction products formed. The way in which the metal compound is introduced into the catalytic circuit is extremely important: the coordination compound is either deposited on the electrode surface or dissolved in the electrolyte.

c. The reduction of CO_2 to CO_3^{2-} and CO

Carbon monoxide is a valuable raw material for the synthesis of organic compounds. For example, methanol can be obtained from carbon monoxide in good yield by electrocatalytic reduction under mild conditions.[174] Organic acids can be obtained by electrocatalytic reduction from unsaturated compounds, CO, and water in the presence of platinum complexes.[172] Finally, the electrocatalytic reduction of carbon monoxide in aqueous solution is of considerable importance for the production of "synthetic gas".[175]

The electrolytic reduction of carbon dioxide to carbon monoxide and carbonate ion takes place as follows:[150]



In the electrolytic reduction of carbon dioxide at a mercury electrode in acetonitrile containing KNO_3 or $LiClO_4$ as background, carbon monoxide is not formed in the absence of a catalyst at -1.6 V. When tetra-aza-macrocyclic derivatives of divalent cobalt and nickel complexes are added to the electrolyte, the reduction of CO_2 to CO takes place at -1.3 V with a current efficiency of up to 90%.[145] In the presence of a catalyst but in the absence of water, carbon monoxide is not formed. The electrocatalytic behaviour of the complex $Ni^{2+}L_2$, where L_2 = 1,4,8,11-tetra-azacyclotetradecane, has been studied.[176] At an Hg electrode in an electrolyte consisting of an MeCN + H_2O mixture, or in an aqueous medium in the presence of this complex, carbon monoxide is formed from CO_2. The authors cited[176] relate the formation of CO in aqueous solution to the geometry of the macrocyclic ligand, which creates round the metallic centre a hydrophobic space or "aprotic niche", which does not prevent the approach of CO_2 to the metal but which hinders the approach of moisture. Of the large number of divalent nickel complexes studied, only dicyclic compounds of nickel were found to be active, and complexes of nickel with unsaturated macrocyclic ligands or with open chains are inactive in this process. In the opinion of Pearce and Pletcher,[132] the fact that no formic or oxalic acid is formed in electrocatalytic processes involving nickel and cobalt chelates is due to the fact that this process takes place by the following mechanism:

$$[LM^{I}]^{n+} + \bar{e} \rightleftarrows [LM^{I}]^{(n-1)+},$$

$$[LM^{I}]^{(n-1)+} + CO_2 + Na^+ \rightleftarrows [LM^{III}CO_2^-Na^+]^{n+},$$

$$[LM^{III}CO_2^-Na^+]^{n+} + H_2O \xrightarrow{\text{rapidly}} [LM^{III}CO_2H]^{n+} + NaOH,$$

$$[LM^{III}CO_2H]^{n+} + \bar{e} \rightarrow [LM^{II}CO_2H]^{(n-1)+},$$

$$[LM^{II}CO_2H]^{(n-1)+} \xrightarrow{\text{slowly}} [LM^{II}]^{n+} + CO + OH^-,$$

$$2\,NaOH + 2\,CO_2 \rightarrow 2\,NaHCO_3,$$

where M = Co or Ni, and L represents the macrocyclic ligand.

According to the data of Tinnemans and co-workers,[177] the complexes of cobalt and nickel with tetra-aza-macrocyclic ligands are effective electron acceptors (first stage). The next stage, according to the above scheme, involves the formation of an adduct with carbon dioxide, in which an alkali metal atom also takes part (bifunctional catalysis). The products of the insertion of CO_2 at a transition metal–alkali metal etc. bond were examined in sections III and IV. The metal-carboxylic acid formed at the stage of protonation of the coordinated CO_2 molecule may be stable even in aqueous media.[36] Nickel-carboxylic and cobalt-carboxylic acids are unstable.[36]

The formation of a complex of carbon dioxide with a Co^{2+} complex obtained by the electrolytic reduction of a Co^{3+} chelate has been described.[178]

The reduction of carbon dioxide to the monoxide in aqueous media can be carried out at a graphite electrode modified by the deposition of cobalt phthalocyanine.[175] The electrocatalytic reduction of CO_2 on this electrode in a citrate buffer at pH 5 takes place at -1.0 V (standard calomel electrode). The efficiency of the electrolytic reduction of CO_2 is sufficiently high only when cobalt phthalocyanine is deposited on the electrode surface; when it is added to the electrolyte, the system has a low catalytic activity, and the results are not reproducible. The potential for the reduction of carbon dioxide is lowered considerably in the presence of complexes of metals with sulphonated phthalocyanines at an amalgamated platinum electrode.[179] In this case the reduction of CO_2 involves two stages; in the first, a complex of the metal with carbon dioxide is formed on the electrode surface, and in the second, an electron is transferred to the CO_2 molecule from the electrode via the transition metal complex.

The electrocatalytic reduction of carbon dioxide to CO also takes place in the presence of bipyridyl complexes of rhenium[180] and ruthenium.[181,182] Thus selective formation of carbon monoxide takes place in the electrolytic reduction of CO_2 in the presence of (bipy)$Re(CO)_3Cl$ in DMF–water (9:1) solution at a glass electrode at -1.25 V (normal hydrogen electrode).[180] The absence of other carbon-containing reduction products was confirmed by ^{13}C NMR. Carbon dioxide is reduced in the presence of the cationic complex of ruthenium $(bipy)_2Ru(CO)_2^{2+}$ in DMF–H_2O solution at -1.5 V (saturated calomel electrode) at an Hg electrode.[181] When the concentration of water in the electrolyte is high, formic acid is also produced. The processes taking place in the electrocatalytic reduction include the formation of an unstable adduct of ruthenium with carbon dioxide:[181]

$$(bipy)_2Ru(CO)_2^{2+} \underset{-OH^-}{\overset{+OH^-}{\rightleftharpoons}} [(bipy)_2Ru(CO)(CO_2H)]^+ \underset{-OH^-}{\overset{+OH^-}{\rightleftarrows}}$$

$$\rightleftarrows [(bipy)_2Ru(CO)(CO_2^-)]^+ + H_2O.$$

Carbon monoxide is liberated with a high current efficiency, together with methanol and methane, at a ruthenium electrode deposited on a carbon electrode at $-(0.35-0.65)$ V (normal hydrogen electrode).[183] CO is also formed in the electrolytic reduction of CO_2 in the presence of sulphur-containing iron clusters.[184] Carbon monoxide and carbonate ion are formed by the photoelectrocatalytic reduction of CO_2 in aqueous solutions at an electrode of the semiconducting *p*-GaAs at -1.2 ± 0.1 V (normal hydrogen electrode)[185] (see next section).

The preparation of CO by the reduction of the hydrogen carbonate ion by a bipyridyl complex of cobalt(I) in aqueous solution at pH 8.5–10.0 has been studied.[186] The carbon monoxide formed reacts with the bipyridyl complex of cobalt to give the stable complex (bipy)$Co(CO)_2$, which has been isolated. Small quantities of formate ion were also produced. The results indicate that the reaction of H_2O and HCO_3^- with $(bipy)_3Co^+$ involves the intermediate formation of the hydride complex of cobalt $(bipy)_2Co(H_2O)H^{2+}$.

Thus the electrocatalytic reduction of CO_2 to CO and CO_3^{2-} differs significantly from the electrolytic reduction of this molecule at smooth electrodes. The study of the electrocatalytic reduction of carbon dioxide in aqueous media involves considerable difficulties, due primarily to the fact that the stages involving the protonation of the coordinated CO_2 molecule, the formation of complexes with carbon dioxide from the metal-carboxylic acids, and the reaction of the hydroxo-complexes with CO_2 have been insufficiently studied, and also to the lack of detailed information on the behaviour of the hydrogen carbonate ligand at the metallic centre, etc.

d. The reduction of CO_2 to formic acid

Formic acid is a product of the reaction of the radical-anion $CO_2^{\cdot-}$, formed by the electrolytic reduction of carbon dioxide, with water or other proton sources in the electrolyte.[2] Among the methods for obtaining HCO_2H, a unique place is occupied by the electrocatalytic reduction of CO_2.

Formic acid is produced by the electrocatalytic reduction of carbon dioxide at a graphite electrode on which the phthalocyanines of cobalt, iron, or copper have been deposited.[187] The highest yields of HCO_2H are obtained when cobalt phthalocyanine is used. This result does not agree with earlier data, according to which oxalic and

glycollic acids, but not formic acid, are produced in the presence of metal phthalocyanines deposited on a graphite electrode.[188] A later study of the behaviour of metal phthalocyanines on an electrode surface showed that formic acid is produced at pH 3.7.[189] In less acidic solutions, the catalytic system in inactive. It was also found that the cathode current increases linearly with increase in the carbon dioxide concentration. The activity of the metals in this process decreases in the order Co^{2+}, $Ni^{2+} \gg Fe^{2+} \simeq Cu^{2+} > Cr^{3+}$.[189] In the electrocatalytic reduction of CO_2 in the presence of cobalt phthalocyanine, small quantities of methanol were detected.

The formate ion is produced in acetonitrile at a graphite electrode on which the complexes of rhodium or ruthenium with 2,6-bis-(2-pyridyl)pyridine have been deposited.[190] When the rhodium complex is used, the electrolytic reduction of CO_2 takes place at -1.55 V (saturated calomel electrode) and gives HCO_2^- (current efficiency 64%) and H_2 (current efficiency 12%), and in the case of ruthenium, formate ion and CO are produced at -1.4 V. It was suggested that an important role in the catalytic act is played by the polypyridyl ligand, acting as an "electron reservoir'. In the electrolytic reduction of CO_2 for a short time interval at a mercury electrode in acetonitrile containing the dissolved complex $(dppe)_2RhCl$, formate is produced with a current efficiency of 42%; with increase in the reduction time, the yield of formate decreases.[191] It is suggested that a complex of rhodium with carbon dioxide is formed during the reaction; this complex in turn reacts with the proton donor to form a hydride, which takes part in the transfer of hydrogen to the coordinated CO_2 molecule.

The electrocatalytic reduction of carbon dioxide has been carried out at a mercury electrode in DMF containing dissolved sulphur-containing iron clusters $[Fe_4S_4(SR)_4]^{2-}$, with R = $PhCH_2$ and Ph.[192] In the presence of these clusters, with a corresponding lowering of the potential, only formic acid is produced, whereas in the absence of the catalyst the main product is oxalate, formed with a current efficiency of 73% (formate ion and carbon monoxide are also obtained, with current efficiencies of 12% and 13% respectively). The authors cited[192] suggest that the source of hydrogen in the synthesis of HCO_2H is the organic radical Bu_4N^+, used as background.

Electrocatalytic reduction always occurs with the formation of a hydride complex, which takes part in the transfer of hydrogen to the CO_2 molecule coordinated to the metal.[191] In principle, the hydride complexes can be formed in two ways:

$$[M] + H_2O \rightleftarrows M(H)OH,$$
$$2[M] + H_2O \rightleftarrows [M]OH + [M]H.$$

Finally, it may be noted that the electrocatalytic reduction of carbon dioxide may involve a fairly complex chain of processes. Thus the preparation of sugars and aminoacids in aqueous solutions has been carried out by creating a catalytic chain in which the photosynthetic stage is replaced by the electrochemical reduction of $NADP^+$ (nicotinamide phosphate) in the presence of ferredoxin or methylviologen to bring about the electron transfer from the electrode to $NADP^+$.[138] The closure of the catalytic ring is achieved by the regeneration of NADPH by electrolytic reduction.

3. The photoelectrocatalytic reduction of carbon dioxide

a. Photoreduction at electrodes of semiconducting materials

The ability of various semiconductors (TiO_2, *p*-GaAs, etc.) to transform light energy into a photo-current has been used, in particular, to reduce carbon dioxide in aqueous solutions.[136] The photoreduction of CO_2 in these media is closely related to the photocatalytic decomposition of water.[193] The solution of the problems of transforming solar energy into electrochemical energy depends to a large extent on the development of studies in this field.[194–196] The efficiency of the transformation of solar into electrical energy on single crystals of *n*-GaAs and *p*-InP reaches 12%.[197]

The photo-process taking place when a quantum of light acts on a semiconductor reduces to the transfer of an excited electron from the valence band of the semiconductor to the substrate. Thus on the irradiation of electrodes to *p*-GaP [198] and *p*-GaTe [199] in the presence of CO_2, the radical-ions $CO_2^{\cdot-}$ are formed on the surface of the photo-cathodes. Carbon monoxide has been obtained from CO_2 at an *n*-CdTe photo-cathode in DMF or MeCN containing small quantities of water.[200] The replacement of Bu_4NClO_4 as electrolyte by NH_4ClO_4 has a marked influence on the magnitude of the photo-current.[201] In the mechanism proposed for the reaction, the ammonium ion transfers the electron to CO_2. CO is formed with a current efficiency of 80% from CO_2 at electrodes of CdTe, GaAs, GaP, and InP in DMSO, DMF, or propylene carbonate.[202] In contrast to the electrolytic reduction of CO on In, Pb, and Hg (see previous section), the reduction of CO_2 on photo-cathodes takes place at potentials between -0.7 V and $+1.0$ V.

In the photo-reduction of CO_2 in aqueous solutions at GaP and GaAs electrodes, the main product is HCO_2H with a small quantity of H_2CO and MeOH. The highest current efficiency of 80% is achieved at a CO_2 pressure of 8.5 atm and a potential of -1.0 V (silver reference electrode). The potential of the cathodic photo-current changes linearly with increase in the pressure. The formation of HCO_2H with a current efficiency of 1% has been observed in the photo-reduction of CO_2 at GaAs in an electrolyte containing the redox system V^{2+}/V^{3+} to prevent photo-corrosion.[204]

Carbon dioxide is reduced to H_2CO, MeOH, and HCO_2H when a *p*-GaP photo-cathode is irradiated with an Hg lamp at pH 6.8.[205] The accumulation of HCO_2H and MeOH at room temperature was observed for 18–90 h. The maximum efficiency of the formation of H_2CO and MeOH when monochromatic light (365 nm) is used has the values 5.6% and 3.6% respectively. For illumination with sunlight, the efficiency decreases to 0.97% and 0.61% respectively. Methanol, CO, and H_2 were detected on the irradiation of a solution of hydrogen carbonate at a GaP photo-cathode using Hg, Xe, and W halide lamps.[206] The addition of crown ethers to lithium carbonate solution in the photo-reduction of CO_2 on GaP increases both the photo-current and the current efficiency of H_2CO, HCO_2H, and MeOH. It has been suggested that the metallic lithium liberated in the presence of the crown ethers reacts with CO_2 to give $CO_2^{\cdot-}$.

Methanol is also formed in the photo-reduction of CO_2 on *p*-GaAs and *p*-InP in an electrolyte containing sodium sulphate.[198] The density of the photo-current and the current efficiency of MeOH depend significantly on the type of electrolyte. The irradiation of CO_2 with monochromatic light in 0.5 M H_2SO_4 on *p*-GaP at -1.5 V gives formaldehyde and methanol.[207] With a disc electrode in the form of a single crystal of *p*-GaAs (As 111) at pH 4.2, the current efficiency of MeOH in the reduction of CO_2 reaches 10% at a current density of 1.4×10^{-4} A cm^{-2}.[185] Increase in the current density leads to a decrease in the yield of MeOH. A study of the influence of the deposition on the *p*-GaP photo-cathode of films of metals with a high hydrogen liberation overvoltage (Pb, Zn, Au) showed that when a Pb film is used, the chief product of the reduction of CO_2 is HCO_2H with a current efficiency of 42%, and the yield of this product is ten times lower at a cathode without a

coating.[208] When the cathode is coated with a Zn film, the main product is CO with a current efficiency of 18%. In both cases, H_2CO and MeOH were not detected in the reaction products. Irradiation with an Xe lamp at a *p*-type silicon photo-cathode alloyed with boron gives HCO_2H (current efficiency 28%) and H_2CO (19%),[207] and the photo-irradiation of CO_2 on photo-electrodes of TiO_2 and titanates containing 0.05–0.5 wt.% added Mn, Fe, Co, and Nb gives H_2CO and MeOH.[208] An apparatus for the photo-initiation of the reaction of CO_2 with water, adsorbed on the [111] face of strontium titanate, on irradiation with an Hg lamp has been described.[209] The products of this reaction include not only methane but also other hydrocarbons, HCO_2H, H_2, and O_2. In the monochromatic (752 nm) irradiation of a *p*-GaP electrode in $MeCN-H_2O$ solution containing tetra-aza-macrocyclic metal complexes, the potential for the reduction of CO_2 is 0.6 V lower than that on metallic electrodes in the presence of the corresponding catalysts.[210]

A laboratory photocatalytic cell for the preparation of HCO_2H from CO_2 using solar energy has been proposed.[211] The efficiency of the cell depends markedly on its design, particularly if the anode and cathode compartments are separated.

Finally, it should be emphasised that an extremely important characteristic of semiconducting photo-electrodes is their ability to reduce CO_2 under "dark" conditions by the creation of a reserve of electrons on preliminary illumination of the photo-cathode.[205,212]

b. Photo-reduction in suspensions of semiconducting materials

The photoelectrocatalytic reduction of carbon dioxide can also be carried out using semiconducting materials in the form of suspensions and colloids. In these systems, the particles of the semiconductor can be regarded as microphoto-electrodes, since the action of light on the surface of the particles produces regions capable of acting as cathodes and anodes. A systematic study of the reduction of CO_2 in aqueous solutions in the presence of suspensions of S, C, CdS, GaP, ZnO, TiO_2, and WO_3 has been carried out.[213] H_2CO and MeOH are formed in the reduction. The yield of MeOH correlates with the potential of the conductivity band of the semiconducting material; catalysts for which the potential is more negative are more effective. Formaldehyde is produced in the presence of suspensions of TiO_2 and calcium and strontium titanates.[214,215] The addition of ruthenium dioxide to TiO_2 leads to the more complete transformation of solar into electrochemical energy, compared with the use of niobium and uranium oxides.[216] The reaction products are H_2CO, MeOH, and HCO_2H. Formaldehyde is produced on the irradiation with an Hg lamp of TiO_2 suspensions covered with films of Pt, Au, Ag, Hg, Co, or Pb.[217] The highest yield is achieved when Hg films are used. Although mercury is oxidised during the photo-reduction, the reverse reduction of mercury oxide to the metal takes place at $\lambda = 600$ nm. H_2CO, HCO_2H, MeOH, MeCHO, and EtOH were obtained from CO_2 and water by the irradiation with an Hg lamp of strontium titanate containing the added oxides of Rh, Ir, Pt, and Ru.[218] The addition of 0.5% $LaCrO_3$ to this system increased the yield of MeOH three-fold. HCO_2H is formed from CO_2 on the irradiation of a suspension of $BaTiO_3$ containing added lanthanide oxides.[219]

An assembly has been proposed[220] for obtaining organic products by irradiation of a CO_2-H_2O-photo-activator (titanates) system. When Li_2CO_3 is added to this system, the degree of transformation of solar energy reaches 0.011–0.016%. The reaction $CO + H_2O \rightleftarrows CO_2 + H_2$ taking place when a TiO_2 suspension is irradiated with an Hg lamp has been studied.[221,222] In particular, it was found that the rate of this reaction is proportional to the light intensity. The preliminary reduction of TiO_2 with molecular hydrogen leads to a marked increase in the photocatalytic activity of the oxide.[223]

4. The photochemical and photocatalytic fixation of carbon dioxide

The problem of obtaining organic products from CO_2 and water under the influence of different forms of radiation is directly related to the study of chemical evolution on the Earth.[2,224] The progress made in recent years in the activation of CO_2 and H_2O by systems based on transition metals has also made a significant contribution to the development of these studies. Early studies examined mainly the effect of ultraviolet irradiation on the CO_2-H_2O system,[2,225–234] to which compounds of transition metals or uranium were added in some cases. Systematic studies[230–234] showed that the ultraviolet irradiation of the CO_2-H_2O system gives CO, HCO_2, H_2CO, and MeCHO. The yield of the photolytic reaction products increases slightly in the presence of Fe^{2+} ions. When aqueous solutions containing CO_2 in the presence of Fe^{2+} were irradiated using a lamp with a power of 375 W (365.5 nm), the formation of oxalic, acetic, and malonic acids was observed. Fe^{2+} ions are usually added to the photolytic system to stabilise $^{\cdot}OH$ radicals.[2] It is possible that they also stabilise $CO_2^{\cdot-}$ radical-anions, which according to the data obtained[230–234] are formed in the photolytic system being considered. In the photolysis of CO_2 using light with arbitrary wavelength, the principal products are CO, O, and small quantities of ozone.[224] The photolysis of carbon dioxide in the presence of metallic mercury gives CO_3,[2] probably via the intermediate $Hg.CO_2$.

Since water and CO_2 do not absorb visible light, a photocatalytic process in this case is possible only when a photosensitiser capable of transferring its absorbed energy to CO_2 and H_2O is added to the system. If the lifetime of the photosensitiser in the excited state is insufficient for the transfer of a quantum of light, the photocatalytic act may be brought about by the introduction of a special agent to transfer an electron from the photosensitiser to the CO_2 molecule. Photocatalytic systems of this type containing a photosensitiser and electron-transfer agents have recently been detected and studied. Thus in the presence of bipyridyl complexes of ruthenium and cobalt, the photocatalytic decomposition of water by visible light can be brought about, with further transformation involving CO_2, by two different paths.[186] The first path can be represented as follows:

$$Ru^{2+} \xrightarrow{h\nu} {}^{*}Ru^{2+},$$

$$^{*}Ru^{2+} + AH^- \rightarrow Ru^+ \ (AH^- \text{ represents the ascorbate ion}),$$

$$Ru^+ + Co^{2+} \rightarrow Ru^{2+} + Co^+,$$

$$Co^+ + H_2O \rightarrow Co^{2+} + {}^1/_2H_2 + OH^-.$$

The Co^+ ion by itself undergoes practically no reaction with CO_2, but in the presence of bipyridyl it becomes a strong reducing agent:[186,235]

$$2(bipy)_3Co^+ + HCO_3^- + H_2O \rightarrow 2(bipy)_3Co^{2+} + CO + 3OH^-,$$

$$(bipy)_3Co^+ + CO \rightarrow {}^1/_4[(bipy)Co(CO)_2]_2 + {}^1/_2(bipy)_3Co^{2+} + bipy.$$

It can be seen from this scheme that the bipyridyl complex of ruthenium acts as the photosensitiser, and the bipyridyl complex of Co acts as the electron-transfer agent. The chief product is CO, but in the pH range 5–10, H_2 and small quantities of HCO_2H are formed.

The second path is represented by the scheme:

$$Ru^{2+} \xrightarrow{h\nu} {}^{*}Ru^{2+},$$
$${}^{*}Ru^{2+} + Co^{2+} \rightarrow Ru^{3+} + Co^{+},$$
$$Ru^{3+} + NTE \rightarrow Ru^{2+} + NTE^{\cdot+} + NTE \rightarrow NTE^{\cdot} + NTEH^{+},$$
$$NTE^{\cdot} + Co^{2+} \rightarrow \text{products} + Co^{+},$$
$$Co^{+} + H_2O \rightarrow Co^{2+} + {}^{1}/_{2}H_2 + OH^{-},$$

where NTE = 2,2′,2″-nitrilotri(ethanol).

The variety of functions which can be carried out by cobalt ions in catalytic systems was noted above; they bring about the decomposition of water,[76] form an adduct with CO_2 in electrolytic reduction,[36] are involved in the formation of cobalt-carboxylic acids,[1,36] etc.

HCO_2H is formed in the photocatalytic reduction of CO_2 in water on irradiation with an Hg lamp with a light filter (λ = 320 nm) in the presence of the system $(bipy)_3Ru^{2+}$ – methylviologen (MV) – triethanolamine (or ethylenediaminetetra-acetic acid).[236] The process involves the MV^{+} radical-cation, which in turn is the product of electron transfer from the photo-excited ruthenium complex. The formation of HCO_2H was confirmed using labelled $^{13}CO_2$.[237] It was also shown that the photolysis involves the formation of ruthenium(I), which reacts with water to give a hydride involved in the formation of the complex with CO_2.

The influence of bipyridyl and 1,10-phenanthroline on the photocatalytic behaviour of M^{2+} ions (Ru, Fe, Co, Cr) on the ultraviolet irradiation (254 nm) of the CO_2-H_2O system has been studied.[238] MeOH and H_2CO are formed in the presence of Fe, Co, and Cr ions. The formaldehyde obtained can be further reduced to MeOH and CH_4.

CO_2 has been reduced to CO in visible light in the presence of $(bipy)Re(CO)_3Cl$ in NTE–DMF solution.[239] Depending on the amine, the photocatalytic system is capable of up to 50 cycles. An attempt has been made to use the photochemical reaction

$$Na_2Ru_3(CO)_{11} \xrightarrow{h\nu} Ru(CO)_5$$

to close the catalytic chain in the production of CO and CO_3^{2-} from CO_2:

$$Ru(CO)_5 \xrightarrow{h\nu} Ru_3(CO)_{12} \xrightarrow{2Na^{+}} Na_2Ru_3(CO)_{11} + CO_2$$
$$\uparrow \qquad\qquad (CO;\ CO_3^{2-}) \qquad\qquad \uparrow$$

The $Ru_3(CO)_{12}$ obtained photochemically was found to be inactive, however.[240]

The ultraviolet irradiation of the CO_2-H_2O system in the presence of luminophors gives H_2CO, oxalic acid, and traces of HCO_2H.[241] H_2CO has been obtained from CO_2 in water in the presence of WO_3, Fe_2O_3, and Hg.[214,215] Formaldehyde has also been detected when CO_2 in water was irradiated with visible and ultraviolet light in the presence of molybdenum compounds.[242] H_2CO, oxalate ion, etc. are formed at room temperature and atmospheric pressure in the presence of the catalyst $TiCl_3$ deposited on a zeolite.[243] The addition of Cr^{2+}, V^{2+}, and Mo^{5+} ions and reducing agents in the form of Mg, Zn, and Al powders have a significant influence on the yield of the photo-reaction.

5. The radiation-catalytic reduction of CO_2 in water

Questions related to the radiolysis of small molecules have been reviewed.[244] According to the data of Getoff,[245] the main products in γ-radiolysis are radicals. In the γ-irradiation of CO_2 in the presence of Al_2O_3 and ZnO, carbon monoxide is formed,[246,247] and in the presence of titanium dioxide, the products are H_2CO, $H_2C_2O_4$, and HCO_2H.[248–250] Increase in pressure from 10 atm to 50 atm has no significant influence on the yield of H_2CO, but the yield increases in the presence of added molybdophosphates. The preliminary γ-irradiation of titanium and zirconium oxides has a significant influence on the nature of the radiation-catalytic process.[248] The radiation-chemical yield (RCY) of the reaction products also depends on the irradiation dose. Formic and oxalic acids and H_2CO have been obtained by the γ-irradiation of homogeneous aqueous solutions of molybdophosphates in a CO_2 atmosphere.[251] Their RCY is influenced by the pH of the medium, the addition of Mg and Al powders, the catalyst concentration, and the irradiation dose. The γ-irradiation of a suspension of $MgCO_3$ in water gives formic, oxalic, and glycollic acids, H_2CO, and other unidentified organic products.[252] The addition of TiO_2 to this system increases the yield of oxalic acid relative to the other products. The nature of the products formed on the γ-irradiation of various carbonates depends on the nature of the cation. Thus the yield of H_2CO in the irradiation of malachite in water is ten times than on the irradiation of Tl_2CO_3. When $MgCO_3$ in water was irradiated with X-rays, H_2CO, HCO_2H, and glycollic acid were not detected, whereas the yield of oxalate was much greater than on the irradiation of other carbonates.[252] The formation of organic products from carbonates in aqueous solutions on different forms of irradiation is of considerable importance for an understanding of questions related to the carbon cycle in nature. The reactions taking place on the γ-irradiation of carbonates provide models of the processes taking place in nature (biogeological catalysis). The minerals taking part in these processes may provide a source of carbon for organic synthesis, and may also provide catalysts for the synthesis of organic substances from inorganic compounds, in particular CO_2 and H_2O.

VI. Summary

The preparation of stable complexes of transition metals with CO_2, which represent a new class of coordination compound, has led to the development of catalytic systems in which carbon dioxide is used as a source of carbon for organic synthesis. This in turn has led to the appearance and development of electrocatalytic, photocatalytic, and radiation-cataiytic methods for the fixation of carbon dioxide. The interest in the problem of CO_2 fixation is due to the role played by carbon dioxide as an inexhaustible source of carbon for the production of fuel and foodstuffs. The results of the studies examined in the present review indicate an increasing interest in this problem from specialists in coordination chemistry, catalysis, electrocatalysis, photocatalysis, bioinorganic chemistry, etc. The solution of the problems of the fixation of carbon dioxide and its use to obtain organic compounds undoubtedly depends to a large extent on the development of combined physicochemical methods for the activation of the CO_2 molecule.

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Control of the efficiency, selectivity, and capacity in single-column capillary gas chromatography

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ABSTRACT. The present review examines published data on a key problem related to the control over wide limits of the efficiency of separation of the components of complex mixtures in single-column capillary gas chromatography and the selectivity and capacity of the capillary columns. Methods of varying these important parameters of the gas-chromatographic experiment, based on the selection of capillary columns of different types and changes in the conditions of the experiment, have been examined in relation to one another and to their influence on the operational characteristics of the capillary columns and the analysis time. The advantages, disadvantages, and ranges of application of different methods for varying the parameters of efficiency, selectivity, and capacity have been noted, and methods for their further improvement in capillary gas chromatography have been indicated.

The bibliography contains 291 references.

Contents

I. Introduction 361
II. The efficiency of separation in single-column capillary gas chromatography and methods for increasing it 361
III. The influence of various factors on the selectivity and capacity of capillary columns 365
IV. Summary 372

I. Introduction

Capillary gas chromatography (CGC) has found extensive application primarily as a method for analysing multicomponent mixtures. In recent years this method has been used to study complex mixtures containing hundreds or thousands of components belonging to different classes of chemical compound, whose boiling points sometimes differ by hundreds of degrees.[1–21] The analysis of these mixtures is often complicated by the fact that the concentration of the components to be determined varies over extremely wide limits from micro-quantities to several tens percent.[1–6,9–13,16]

In relation to these characteristics of the specimens being analysed, it is possible to distinguish three main groups of problem encountered at the present stage of development of CGC.

The first group of problems is related to the resolving power of the columns, the reliability of the results of the analysis, and the sensitivity of the method, and solutions are sought by improving the efficiency, selectivity, and capacity, and also by using highly sensitive detectors and by improving the methods used to introduce the specimens into the chromatograph.[1–8,12,14,16,20–46] The problems of the second group are associated with the identification of a wide range of components, many of which are present in extremely low concentrations.[7,8,12,15,16,35,45,47–49] The solution of the problems of these two groups is inseparable from problems associated with the improvement and the development of new methods for the treatment of chromatographic information, making it possible to increase both the reliability of the identification of the components and their quantitative determination and also the amount of detail in the data on composition obtained.[17–19,50–54] The third group of problems is related to the development and application of multi-column gas-chromatographic systems which make it possible to decrease the total time taken for determinations without decreasing the reliability and amount of detail in the information obtained.[7–13,16,18,55–66] In a number of cases the use of these systems makes it possible to increase considerably the sensitivity of the determination of micro-quantities by using large specimen volumes.[11–13,62]

The present review examines the problems of increasing the efficiency of separation in single-column CGC and the selectivity and capacity of the capillary columns (CC). In fact, the problem reduces not to the optimisation of each of these characteristics but to the optimisation of the separation factor R_s. In many cases, the requirements relating to the individual parameters may contradict one another, that is the improvement of one characteristic may lead to a simultaneous deterioration in another. To simplify the systematisation, however, it is appropriate to examine the optimisation of each of these characteristics separately.

II. The efficiency of separation in single-column capillary gas chromatography and methods for increasing it

Capillary gas chromatography originated with Golay's discovery in 1956–1957 of open CC whose internal surface was covered with a layer of a stationary liquid phase (SLP).[1,3,6,35,67–69] This discovery marked a qualitatively new giant step towards a sharp increase in the efficiency of gas-chromatographic separations in general. The very first studies, carried out using mainly metal, plastic, and glass CC with an internal diameter d_c = 0.2–0.5 mm, demonstrated the extensive possibilities provided by CGC as a result of the high permeability of the CC and their high specific efficiency.[1,3,6,35,67–71] The use of even very long CC (100 m or more) removes the need to use extremely high inlet pressures, and in practice this makes it possible to achieve a very high efficiency of separation, reaching 1 million theoretical plates (t.p.) or more.[1,3,6,35,67–71] The unique possibilities provided by CGC as a powerful method for the fine separation of complex mixtures are demonstrated particularly clearly by the chromatogram obtained for petrol, with 378 separate peaks,

obtained on a CC (300 m × 0.5 mm) containing squalane.[14,15] Only 17 of these peaks belong to unidentified components. This chromatogram is the most complete chromatogram for petrol known at present.

1. Methods for increasing the efficiency of separation based on the use of capillary columns of different types

a. Treatment of the internal surface of glass CC

In the initial stages of the development of CGC, the specific efficiency of CC was 1000–2000 t.p. m^{-1}.[1,3,6,67–71] The development of various methods for the preliminary treatment of the internal surface of glass CC (deactivation, treatment with surface-active substances, chemical modification, the production of a rough surface, the creation of an intermediate layer of polymeric materials, carbon, salts, etc.)[1–3,6,21,35,68,72–89] made it possible to increase the specific efficiency of glass CC to 3000–4000 t.p. m^{-1}. This was related to the production, by both static and dynamic deposition, of a stable and uniform film of SLP and to the decrease in the adsorption and catalytic activity of the internal surface of the CC with respect to extremely polar compounds.[1,3,6,21,35,68,69,72–86,88,90] CGC on glass CC became an extremely effective method for separating the components of tobacco smoke,[1,3,91] mixtures of various aminoacids and their enantiomers,[1,4,75,92] aliphatic acids,[1,88,91] alcohols,[75,91] esters,[6,88] amines,[75] steroids,[1,3,4,77,88] the components responsible for the odour and taste of various food products and wines,[1,3,4,49,85,88,93] mixtures of pesticides,[1,3,35,85,88] various derivatives of saccharides,[1,88] and other complex mixtures.[1,3,4,6,35,49,68,69,74–80, 85,88,90–94] The increased possibilities provided by CGC are clearly confirmed by the chromatogram for a middle fraction of cigarette smoke, containing more than 3000 components of different chemical character (hydrocarbons, acids, bases, polyalcohols, ketones, etc.), recorded as 1000 peaks; this chromatogram was obtained on a glass CC (145 m × 0.32 mm) containing Emulphor ON 870 with linear temperature programming (1 °C min^{-1} in the range 25–190 °C).[91] The reliable identification of the components of such a complex mixture obviously requires a complex approach using several columns and detectors with different selectivities.[7,8,12,13,16,35,91]

The extensive application of glass CC was facilitated by such factors as the possibility of preparing glass capillaries with a clean internal surface under laboratory conditions and by the ease of visual control of the deposition of SLP films. Other important factors in the application of glass CC at high temperatures include the possibility of observing the stability of the SLP film and the ease of determining the section in which the macromolecular compounds present in the specimens being analysed are deposited irreversibly. Nevertheless, the range of application of glass CC is restricted, because of the residual adsorption activity of the surface with respect to a whole series of chemical compounds, determined to a large extent by the type of glass and the method of treatment; moreover, the mechanical strength of glass CC is too low.[1,3,6,74,75]

b. The use of quartz CC

A new and promising direction in the development of CGC is associated with the use of flexible CC of fused quartz, having d_c = 0.05–0.32 mm and a wall thickness of 40–70 μm.[20,27,28,34,35,39,40, 68,86,95–109] These CC have a high mechanical bending strength, which together with the low adsorption and catalytic activity of their internal surface has led in recent years to the extensive replacement of glass by quartz CC.[20,27,28,34,35,86,95–110] The specific efficiency of columns of this kind with an internal diameter d_c = 0.2 mm approaches 5500 t.p. m^{-1},[109,110] and they can be used to analyse mixtures containing strongly polar and readily adsorbed compounds: polyaromatic hydrocarbons (PAH),[4,100,107–110] alcohols,[27,28,103,109] phenols,[97,109] acids,[97,98,103,109] esters,[27,28,97,98,103,109] anilines, amines, and nitro-compounds,[97,109] pyridines and quinolines,[100,103] peptides and other substances present in biological specimens,[4,111] the components of medicinal products,[28,107] the components responsible for the taste and odour of foodstuffs† and cosmetic materials,[27,28] and many other compounds.[4,105,106,111] Because of their low catalytic activity, quartz CC are used successfully to separate various labile compounds.[97,105,111]

c. The efficiency of separation on CC with a small diameter

In CGC, increasing use is being made of CC with a small internal diameter (d_c = 0.035–0.1 mm).[6,96,104,112,113] It has been shown[104] that the height equivalent to a theoretical plate (HETP), measured for n-pentadecane on a 10-metre quartz CC (d_c = 0.1 mm) containing phenylmethylsiloxane at a medium linear carrier-gas velocity corresponding to the minimum of the Van Deemter curve, is 0.105 mm, which is only 1.08 times the height 0.097 mm calculated from the equation

$$H_{\min} = \frac{d_c}{2}\sqrt{\frac{1 + 6k' + 11(k')^2}{3(1 + k')^2}} \qquad (1)$$

for the theoretical minimum value of the HETP[32,114] [the capacity (extraction) coefficient k' for an SLP film thickness d_f = 0.17 μm and a CC temperature t_{CC} = 143 °C is 6.5]. For a 70-metre CC with d_c = 0.05 mm, the HETP was 0.066 mm.[96]

Short CC of small diameter with a high specific efficiency are characterised by a displacement of the minimum of the Van Deemter curve to high linear carrier-gas velocities (50–70 cm s^{-1}), which, together with the small quantity of SLP in these columns creates a realistic basis for increasing considerably the speed of analysis and the sensitivity of determinations.[6,96,104,112,115] For rapid separation it is appropriate to use hydrogen as the carrier gas.[116] In high-speed CGC using open tubular CC, the record time is 2 s, achieved in the separation of 15 components on a CC (1.2 m × 0.035 mm) with an efficiency of 7000 t.p.[115] It has been suggested that it should be possible to develop a high-speed analyser using a CC with a length of several centimetres and a diameter of 1 μm.[117] In addition to the high speed of analysis, specific efficiency, and sensitivity of the determinations, an undoubted advantage of CC with a small diameter is the low loss of SLP, ensuring stability of operation over a long time.[96,113] The low noise level makes it possible to use CC of small diameter for high-temperature analyses and the determination of traces of substances.[113] Nevertheless, the use of CC of small diameter involves difficulties associated with their low sorptive capacity, so that the size of the specimen calculated for one component is only 0.02–1 ng for a CC with d_c = 0.05 mm,[112] and ~8 ng for CC with d_c = 0.1 mm,[104] and also with the severe requirements to be satisfied by the inertia of the recording apparatus. The limitations associated with the need for a high inlet pressure can be overcome by creating a vacuum at the outlet from the CC, and this in turn favours the use of a mass spectrometer as detector.[104]

† T Aishima, Y Ozawa *Chromatographia*, 1989, **28** 405

The extensive application of CC of small diameter is also prevented at present by difficulties associated with the deposition of viscous high-temperature SLP. This also applies to some extent to CC with a diameter d_c = 0.1–0.25 mm. Static methods for preparing CC using traditional solvents with the boiling points of n-pentane (b.p. = 36.07 °C) and above do not always give CC with high specific efficiency and reproducible values of other gas-chromatographic parameters. This is largely due to the need to use relatively high pressures to fill the CC with the solution of the SLP in the appropriate solvent and special methods for subsequently making the ends of the CC air-tight, which do not always eliminate completely the formation of bubbles of gas and solvent vapour.[1,3,88] Of particular interest is a recently described‡ new method for the static deposition of non-polar and weakly polar SLP on the walls of CC whose internal diameter, according to the authors cited, may be smaller than 0.1 mm. Characteristic features of this method are the use of n-butane (b.p. = –0.5 °C) as solvent for the SLP, and the method used to make one of the ends of the CC air-tight by freezing the solution of the SLP in n-butane with liquid nitrogen in a closed vessel, into which gas nitrogen can be passed at a pressure of 2 atm. This method eliminates completely the formation of gas bubbles at the boundary between the liquid and solid solutions. The solvent (n-butane) is removed from the CC at room temperature and atmospheric pressure. The method developed makes it possible in practically 100% of cases to obtain CC with specified properties with a simultaneous decrease in the time taken for their preparation compared with traditional static methods. In particular, the time taken to prepare a quartz CC (25 m × 0.25 mm) at 30 °C is not more than 5 h, and this is reduced considerably (to tens of minutes) on going to CC with a smaller diameter. Other advantages of the new method for preparing CC can be seen from Table 1, which gives the gas-chromatographic parameters of quartz CC with different geometric characteristics (length L and internal diameter d_c) and different SLP. Table 1 shows, in particular, that the specific efficiency of quartz CC of small diameter (d_c = 0.10 mm), measured from the peak of n-tridecane, is close to 10000 t.p. m^{-1}. The new static method for preparing CC of any diameter should lead to their wider application in gas chromatography.

Table 1. Characteristics of various quartz capillary columns prepared by a new static method.

L, m	d_c, mm	SLP	t, °C	k' (measured from n-C_{13})	n, t.p. m^{-1} (measured from n-C_{13})	Efficiency of deposition, %
14	0.25	SE-54	130	14.4	3900	89
10	0.25	SE-54	130	11.1	3860	87
30	0 25	SE-54	120	9.0	4200	92
25	0.22	SE-30	120	11.5	4270	92
14	0.22	SE-30	120	9.6	4500	89
25	0.22	SE-30	120	3.9	4650	84
12	0.10	SE-54	140	5.2	9310	79
12	0.10	SE-54	120	5.8	8600	73
12	0.10	OV-1	120	5.3	9100	77

d. The influence of the SLP film thickness on the efficiency of separation

Decrease in the thickness d_f of the SLP film in CC makes it possible not only to decrease the analysis time and lower the analysis temperature but also to increase the efficiency of separation by decreasing the contribution of the intra-diffusion resistance and the resistance to mass exchange at the interphase boundaries. This follows directly from the Kahn equation for the HETP in open CC, which, unlike the familiar Golay equation, takes account of the resistance to mass transfer at the interphase boundaries:[3,6,118,119]

$$H = \frac{2D_g}{\bar{u}} + \frac{1 + 6k' + 11(k')^2}{24(1 + k')^2}\frac{\bar{u}d_c^2}{4D_g} + \frac{2k'}{3(1 + k')^2}\frac{d_f^2\bar{u}}{D_l} + \frac{2k'd_f}{(1 + k')^2 k_d} \quad (2)$$

Here, $\bar{u}$ is the average linear velocity of the carrier gas, D_g and D_l the coefficients of molecular diffusion of the sorbate molecules in the gas and liquid phases respectively; and k_d the rate constant of the desorption of the substance from the surface. The first term of this equation describes the contribution to the flattening of the chromatographic band made by the longitudinal diffusion of the sorbate molecules in the gas phase, the second term characterises the contribution of dynamic diffusion, and the third and fourth terms, which contain the quantity d_f, give respectively the resistance to mass transfer in the SLP film and the resistance to mass exchange at the interphase boundaries, which is equivalent to a slight deviation from the equilibrium state.

The existence of the third and fourth terms in Eqn. (2) indicates the strong dependence of the efficiency of separation on the thickness of the SLP film. The role of the film thickness increases for values of $\bar{u}$ greater than the optimum velocity u_{opt}, which corresponds to the minimum of the Van Deemter curve. Overall, however, the influence of d_f on the quality of separation of the components is much more complex, and depends on the capacity coefficient k'.[1,3,6,118,120] It should also be noted that a decrease in d_f carries the danger of overloading the CC.[104,112]

e. The efficiency of micropacked CC

Considerable advantages over open tubular CC in relation to the specific efficiency of separation, capacity, and speed of determination are shown by micropacked quartz capillary columns (MPQCC) having d_c = 0.15–0.5 mm and sorbent particle diameters of 5–100 μm.[121–127] The use of quartz CC with smooth walls simplifies considerably the filling of the column with the sorbent,[121–124,126] making it possible to achieve uniform packing of the latter. Together with the small particle size of the packing, the small internal diameter of the MPQCC, and the inertness of their internal surface, this feature ensures a high specific efficiency for the MPQCC, which for a sorbent particle diameter of 7.5 μm may reach 30000 t.p.[121–125] The high specific efficiency of MPQCC makes it possible to use short columns with typical lengths of tens of centimetres, and hence to reduce the expenditure on scarce and expensive sorbents. An important positive feature of MPQCC is the extremely weak dependence of the HETP on $\bar{u}$ at $\bar{u} > u_{opt}$,[121–123,125] particularly for a sorbent particle size less than 1 mm. This makes it possible to increase considerably the speed of the determination. The use of MPQCC, which makes it possible to miniaturise the equipment, retains all the advantages of open tubular

‡H F Yin, A J Huang, Y L Sun *Chromatographia*, 1989, **28**(5/6) 313

quartz CC, namely their flexibility, mechanical strength, and adsorption and chemical inertness.[121–126]

f. The influence of the length of the CC on the overall efficiency of separation

A radical method for increasing the overall efficiency of CC is by increasing their length. Short CC always have smaller HETP than long columns with identical properties.[116,128] This is related to the large change in the carrier-gas velocity along the length of the CC. Thus the increase in the number of theoretical plates is not directly proportional to the increase in the length of the CC. In practice, the CC used most frequently have lengths not exceeding 50 – 100 mm.[1,6,15,17–21,27–46,52–89,92–109,111–120,128,129] Further increase in the length of the CC is not appropriate, because of the increase in the total analysis time and the decrease in the sensitivity of the determinations as a result of the diffusion flattening of the chromatographic bands. Increase in the length of CC is particularly unjustified when carrying out analyses using CC with a small internal diameter (0.035 – 0.1 mm) or MPQCC, since it leads to a multiplication of the inlet pressure, makes more severe demands on the apparatus used, and also leads to a large pressure drop along the length of the CC, which in the final analysis lowers the overall specific efficiency of separation.[96,104,112,115,116,121–124,128] Moreover, the long analysis time on long CC and the need to increase the column temperature create difficulties in the study of mixtures of substances with a wide range of boiling points, non-volatile substances, and mixtures containing thermally labile and reactive compounds.[1,3,6,116,118]

g. The efficiency of CC with non-circular cross-section

In recent years there has been an increase in interest in open tubular CC with rectangular cross-section,[3,88,90,130–138] whose walls are covered with a thin film of SLP. Under certain conditions, the use of these columns leads to a marked increase in the efficiency of separation compared with CC having circular and elliptical cross-sections. This is related primarily to the significant decrease in the contribution to the HETP made by the dynamic dispersion due to the non-uniform distribution of the carrier-gas velocities over the cross-section of an open CC in a laminary stream. These theoretical postulates[132–138] were confirmed experimentally by comparing the efficiencies of CC having cross-sections with different shapes but identical areas.[133,135,137] In particular, it was shown[136,137] that the efficiency of CC having cross-sections with different shapes depends on the capacity coefficient k' and on the ratio of the sides a and b of the rectangular cross-section. Thus the efficiency of a rectangular CC increases rapidly with increase in a/b and becomes greater than the efficiency of a cylindrical CC at $a/b > 3.5$ (if $k' = 0$) and $a/b > 2$ (if $k' = 2$). The study of the influence on the efficiency of separation of a change in the cross-sectional area of a CC along its length is also of considerable and theoretical and practical interest.[132]

2. Methods for increasing the efficiency of separation based on a change in the parameters of the gas-chromatographic experiment

The main disadvantage of all the above methods for increasing the efficiency in single-column gas-chromatographic systems is the need to replace the CC, which is inconvenient.

a. The influence of the nature of the carrier gas, its average linear velocity, and the average pressure on the efficiency of separation

Among the methods for increasing the efficiency of separation without replacing the CC, mention must be made of readily accessible methods involving a change in the nature of carrier gas, its average linear velocity, and the average pressure.[1,3,6,115,118,119] The first two methods make it possible to change the efficiency of separation only over a narrow range, particularly at $\bar{u} > u_{opt}$.[118,119] An increase in the average pressure of the carrier gas from 1 atom to 10 atm, however, decreases H_{min} by 55% with a simultaneous displacement of the minimum of the Van Deemter curve to low linear velocities,[115] leading to an increase in the analysis time. The use of high pressure also creates experimental difficulties, and all these features make this method inefficient.

b. The use of gaseous mobile phases

An interesting method for increasing the efficiency of separation involves the use in the CC of gaseous mobile phases containing volatile polar substances.[3,6,16,122,139–144] A high efficiency of separation by this method was first achieved using water vapour.[3,140] Water vapour as a modifying additive was subsequently used successfully in a number of other studies.[141,144] Suppression of the adsorption activity of the walls of the CC, leading to the production of symmetrical peaks and an increase in the efficiency of separation of the components, can also be achieved by the constant supply of the vapours of other polar substances such as ammonia,[139] formamide,[143] formic acid,[143] and other compounds which, like water, give practically no signal when the most widely encountered flame-ionisation detector (FID) is used. The addition of these compounds to the carrier gas, which leads to a decrease in the part played by both the reversible and the irreversible adsorption of the compounds, also makes it possible to increase considerably the reliability of the quantitative analysis of the mixtures studied and the reproducibility of the retention parameters of their components.[122]

c. The influence of the method of introducing the specimen, and extra-column effects, on the efficiency of separation

The efficiency of separation in CGC depends to a marked extent on the method of introducing the specimen into the chromatograph.[1–3,6,22–24,27–32,35,36,38,88,93,144,146] To achieve the maximum efficiency of the CC it is necessary to eliminate or reduce to a minimum the unfavourable consequences of various extra-column effects leading to additional spreading of the specimen in the volatiliser of the chromatograph and its connections in front of the CC.[1,3,6,22,29,36,38,88,145,146] It is also important to eliminate overloading of the CC with the components of the specimen, which unavoidably leads to a decrease in the efficiency of separation.[1,3,6,22,23,29,88,104,112,118,119] These requirements are satisfied to a significant extent by the following methods of introducing the specimen: 1, a method based on splitting the stream of carrier gas at a volatiliser temperature equal to or greater than the boiling point of the least volatile component of the specimen;[1,3,6,23,88,104,112] 2, a method based on the so-called "solvent effect";[1,93,145,146] and 3, various modifications of a method involving the cryogenic focussing of the components in the initial section of the CC.[3,25,26,28,35–38,147–152] A high efficiency of separation is also obtained using various versions of the method of cold introduction of the specimen into the CC.[31,32,153] Promising possibilities are

provided by the recently employed method of introducing a liquid specimen with temperature programming of the injector,[29–33] which combines the advantages of the methods involving splitting of the stream of carrier gas and cold introduction.

The use of low-inertia ionisation detectors and mass spectrometers,[3,12,17,21,68,69,118,119,153] and the improvements of methods for combining them with CC[3,21,36] eliminate practically completely the loss of efficiency of separation at the outlet from the CC.[3,12,36,68,118,119,153]

Methods for introducing the specimen also have to satisfy high requirements in relation to the reliability of quantitative analysis,[1,3,23,29,31–34,37,38,113,129,149,150,153,154] the high sensitivity of determinations,[1,3,6,23,28,30,33,35,37,129,145–148,151,152,155] and the high stability of operation of the CC over a long period.[23,32]

III. The influence of various factors on the selectivity and capacity of capillary columns

High efficiency is a necessary but not a sufficient condition for the qualitative separation of components with similar physicochemical properties. This can be seen from the fundamental equation of Purnell.[1,120,122]

$$R_s = \frac{\sqrt{n}}{4}\,\frac{\alpha-1}{\alpha}\,\frac{k'}{k'+1}, \qquad (3)$$

which establishes the relationship between the separation criterion§ R_s,[1,6,119,122] characterising the completeness of the separation of two components, and not only the kinetic parameter (the number of t.p. n, measured from the second component) but also the equilibrium parameters of the chromatographic process—the selectivity coefficient α[1,16,122,] and the capacity coefficient k',[1,88,122] calculated from the second component.

The selectivity coefficient $\alpha \geqslant 1$, which is the ratio of the reduced¶ retention times (volumes) of two components being separated,[1,3,16,88,122] is determined by the partial pressures p_1^0 and p_2^0 of the vapours of these components and their activity coefficients γ_1 and γ_2 in solution in the SLP used:[16,35,156]

$$\alpha = \frac{p_1^0}{p_2^0}\,\frac{\gamma_1}{\gamma_2}, \qquad (4)$$

The quantity α is also called the "separation coefficient"[3,88] or the "separation factor".[1]

The capacity coefficient k' depends on the distribution constant K_L of the component between the liquid and gas phases and the ratio of their volumes $\beta = V_G/V_L$:[1,3,6,118]

$$k' = K_L/\beta. \qquad (5)$$

The quantity k' is sometimes called the "extraction coefficient"[1,3,88,118,122] or the "distribution ratio".[3] This is related to the fact that the capacity coefficient k' is a measure of the time for which the molecule of a given component is in the stationary phase relative to the time t_0 for which it is in the gas phase [$k' = (t_R - t_0)/t_0 = t'_R/t_0$]. In other words, k' is the ratio of the capacities of the stationary and mobile phases.

Analysis of the simple relationships (4) and (5) indicates several possible ways of controlling the selectivity and capacity in gas-chromatographic systems with one CC in the analysis of complex mixtures containing pairs and groups of components which are difficult to separate.

All known methods for controlling the selectivity and capacity in these systems can be divided into two main groups. The first is not associated with replacement of the CC,[1,3,16,35,118,119,122] while the second provides for replacement of the CC.[1,3,7,8,16] The factors influencing the selectivity of the separation of the components also influence the capacity coefficient k'. The converse does not always apply, since with change in the geometric parameters of the CC (L, d_c, d_f), the separation factor α may remain unchanged if the part played by adsorption effects at the phase interfaces in the system is negligible.[122]

1. Methods for controlling the selectivity and capacity parameters without replacing the capillary column

a. Changing the temperature conditions of the analyses

The simplest and most readily available method of varying the selectivity and capacity over wide limits is by changing the temperature conditions of the gas-chromatographic process.[1,3,15–19,21–35,87,118,119] In the analysis of complex mixtures consisting of chemical compounds of different classes, characterised by different temperature dependences of the retention parameters, however, this method is not always effective, since an improvement in the degree of separation of some pairs of compounds may be accompanied by a deterioration in the degree of separation of other pairs.[1,17–19,158] In a number of cases, a change in the temperature of the CC also changes the order of elution of compounds differing in the type and number of functional groups and the molecular framework.[1,17–19,158]

Changing the working temperature of the CC not only influences the selectivity and capacity but also opens up additional possibilities for the group identification of the components of complex mixtures, since the temperature coefficient of the retention index dI/dt depends on the structure of the molecule and the class of compound to which the component being identified belongs.[1,15,16,17–19,47,48,157–169]

Decrease in the temperature of the CC ensures a definite gain in selectivity in the separation of compounds with similar values of dI/dt. With decrease in temperature, in accordance with Eqn. (5), there is a simultaneous increase in the extraction coefficient k' according to a law close to exponential, and this unavoidably leads to a sharp increase in the analysis time.[1,118,119] For this reason, the analysis of mixtures of compounds belonging to the same homologous series and having appreciably different boiling points is carried out with temperature programming of the CC, which makes it possible not only to decrease sharply the separation time but also to increase considerably the sensitivity of the determinations.[1,3–6,15,21,44,53,87,98,108,118,119,157,168,170,171] Temperature programming also has some unfavourable consequences, associated primarily with the unsatisfactory reproducibility of the retention parameters used to identify the components,[6,15,47,48,116,172] possible decomposition of the substances being analysed, deterioration in the stability of the operation of the CC under the influence of the brief

§The quantity R_s is sometimes called the "resolution"[88] or the "degree of separation".[3,35,157]

¶As in the works cited,[6,16,157] the reduced quantities are the equilibrium characteristics of the gas-chromatographic process, calculated using the quantities obtained by subtracting from the gas-chromatographic retention time t_R the retention time t_0 of a non-sorbed component.

application of high temperatures,[1,6,8,118] and the incomplete utilisation of the potential efficiency of the CC.[1]

b. The influence of the composition and pressure of the carrier gas

In some cases the selectivity and capacity of CC can be controlled effectively by varying the composition of the carrier gas by adding to it various volatile readily adsorbed polar substances.[3,16,122,141] These substances dissolve selectively in the SLP and are adsorbed on various active centres of the CC, changing its capacity and selectivity with respect to both polar and non-polar compounds.[3,16,122,141]

The range of change in the selectivity and capacity of CC with change in the composition of the mobile phase can be increased considerably by altering the pressure of the mobile phase. Increase in pressure leads to an increased influence of the non-ideality of the gas phase on the solubility of the components in the SLP and on the retention characteristics.[16,142,173,174] Thus this method makes it possible to vary the selectivity and capacity of CC over wide limits, by controlling the pressure in the CC and the composition of both the mobile and the stationary phase. This is achieved by using vapour–gas mixtures under conditions in which the stationary phase is capable of sorbing the vapour strongly.

The use of gaseous mobile phases with modifying polar additives increases not only the selectivity and capacity of the CC but also, as noted above, the efficiency of separation and the reliability of the qualitative and quantitative analysis of complex mixtures.[3,6,16,35,122,139–144] An important factor is the increase in the sensitivity of the determination with a simultaneous decrease in the analysis time as a result of a decrease in the contribution of adsorption retention centres to the total retention of the sorbates[122] and an increase in the carrier-gas velocity.

An increase in the selectivity with change in the pressure of the carrier gas in CC is achieved even without adding polar additives to the carrier gas. This is particularly characteristic of argon and carbon dioxide, which are appreciably non-ideal at increased pressures.[16,141,142,173,175] This method of varying the selectivity of CC is also of interest for the group identification of components, since the value of $dI/d\bar{p}$, characterising the dependence of the retention index I on the average pressure $\bar{p}$ in the CC, is specific for definite groups of compound and is related to the value of the second virial coefficient in the equation of state of the vapour.[1,173,175] A study of the retention of various aromatic sorbates from benzene to 1,2,3,4-tetramethylbenzene (a total of 31 compounds) on CC with an efficiency of 150–200 thousand t.p. with polyethylene glycol 400 at 80 °C showed that in this series the value of $dI/d\bar{p}$, changes in the range 1.0–1.5 index units per atom[173] (the range of change in the pressure of Ar and CO_2 was 1.2–30 atm).

c. A method for continuously changing the selectivity and capacity

An interesting method for gradually changing the selectivity and capacity is based on the continuous removal from the CC of a volatile component of a binary SLP under isothermal conditions.[7,174] The possibilities provided by the method have been examined for the case of an analysis of petrol on a CC filled with a mixture of FS-16 fluorinated silicone and octadec-1-ene, which is gradually removed at 60 °C.[174] When both components of the binary SLP used are non-volatile at the working temperature, the CC is heated between analyses to remove a definite quantity of one of the phases. This method makes it possible, by examining the set of chromatograms, to establish the regularities of the change in the order of elution of the components of a complex mixture on going from one phase to another and on this basis to compile a binary (two-dimensional) spectrum of the signals relating to each component of the mixture. The method is restricted to a relatively narrow range of control of the selectivity and capacity of the CC, determined by the characteristics of the binary SLP used and its less volatile component, and also by the inadequate reproducibility of the retention parameters.

d. The use of an electric field

An extremely promising method of controlling the selectivity of liquid-crystalline SLP is by applying an electric field.[176] The method makes it possible, by changing the modulus and direction of the electric field intensity vector, to vary over a wide range not only the selectivity of the CC but also its capacity, and even to achieve the complete retention of some components. After the removal of the electric field, the compounds retained in the CC are rapidly eluted with a stream of carrier gas. In this way it is possible to achieve the complete separation of substances showing only extremely small differences in their molecular structures.[35,176] The method is restricted by the need to use liquid-crystalline SLP.

2. Methods for improving the selectivity and capacity by selecting capillary columns with different properties

General advantages of all the above methods for controlling the selectivity and capacity of CC are their simplicity and the possibility of achieving fairly smooth control of these important parameters.[16] Nevertheless, the impossibility in a number of cases of achieving the selectivity and capacity parameters required for the separation of all the components of complex mixtures of organic compounds, and the insufficient reproducibility of the retention characteristics, make it necessary in single-column gas-chromatographic systems to use a succession of several CC with different sorbents and SLP.[6–8,16,18,19,21,47,48,157,177] The possibilities provided by this approach have increased significantly in recent years as a result of the introduction into gas-chromatographic practice of different types of CC,[1,3,6,35,42,68,74,75,86,88,95–108,113,121–125,178–194] and also such SLP as nematic liquid crystals, showing a high selectivity with respect to many pairs of components difficult to separate,[7,35,39–41,66,89,195,196] and chemically grafted,[42,80,88,113,191,192,194,198] immobilised (transverse cross-linked),[35,42,68,102,105,107–109,171,194,197–205] mixed,[86,206,207] and colloidal[122,208,209] SLP.

The successive use of CC with different sorbents and SLP makes it possible to carry out separations using different types of intermolecular interaction, and on this basis to obtain a many-element chromatographic spectrum characterising the retention of the individual components of the complex mixture being analysed on the CC used.[7,8,16,18,19,48,177] To increase the reliability of the identification of the components and decrease the volume of excess information, it is desirable that the elements of the spectrum be as far as possible mutually independent.[7,8,16,18,19,48,177] It is therefore appropriate to reduce to a minimum the number of CC used, in which there is a predominance of definite types of interaction giving a selective separation and the required operational characteristics of the CC, the most important of which are the upper temperature limit (UTL) at which the SLP can be used, the efficiency and capacity of the CC, the stability of its operation over a long period, and the possibility of combining the CC with selective detectors.[1,3,6–8,12,35,46,68,107,113]

The change in the order of separation of components belonging to different classes of organic compound with change in the temperature of the CC and the polarity of the SLP has been successfully used[17–19,177] to identify the components and increase the amount of detail in the information obtained on the composition of complex natural mixtures of hydrocarbons. A method has been proposed[17–19,177] for the treatment of chromatographic data based on the combination of the results of the quantitative analysis of the compounds, determined at different temperatures on one CC, and also on different CC with different selectivities with respect to the same pairs of compound. The applicability of the method, which makes it possible to obtain information on the separate concentrations of components which do not give independent peaks, has been examined for the case of the analysis of specimens with markedly different quantitative compositions, namely broad petrol fractions from low-boiling to 150 °C and unfractionated petroleums and condensates, on relative short 50-metre CC containing squalane[17,18,56] and dinonyl phthalate.[18,19,177] The use of a method for the treatment of chromatograms to give detailed information on the composition of complex specimens identified approximately 200 C_1-C_9 hydrocarbons, and 17 [177] groups of hydrocarbons remained unseparated, whereas on CC with squalane and dinonyl phthalate the number of these groups was 46 and 40 respectively. From the increase in the amount of detail in the information on the composition, the combination of the results of quantitative analysis obtained under different gas-chromatographic conditions is equivalent to the use of long CC at low temperatures. This unavoidably leads, however, to a multiple increase in the analysis time and to a considerable decrease in the sensitivity of the determinations. In the works cited,[17–19,177] the results of the quantitative analysis of complex organic mixtures were used for the first time in gas chromatography to identify their components.

a. The production of a highly developed internal surface in CC

Various methods have been described for preparing CC with a high sorptive capacity. The nineteen-sixties saw the beginning of the intensive development of methods for the treatment of the internal surface of glass CC by etching it and giving it different types of roughness,[1,3,6,35,68,73,77,80,81,84,88,186,210] and also by forming on it thin layers of crystals of different substances[1,3,6,68,73,80,83,211] and whiskers.[1,6,68,73,76,81,84] The surface obtained in this way is readily wetted by a thick layer of both polar and non-polar SLP. Despite the high stability of the CC obtained,[1,83] they have a low efficiency, since the porous layer formed by etching has an extremely strong adsorbing power,[1,6,77,88] leading to the production of unsymmetrical chromatographic zones. Salt crystals formed on the internal surface of CC are also unstable to water vapour.[6,212] These features restrict considerably the application of glass CC with a highly developed surface in gas–liquid chromatography, and in a number of cases it is necessary to carry out subsequent operations to deactivate the surface.[1,3,6,88] These CC are fully applicable, however, in gas-adsorption chromatography.[6,77,88]

b. Columns with a porous layer of sorbent

The disadvantage of CC with a highly developed surface, noted above, led to the development of open capillary columns (OCC) containing a porous layer of sorbent on the internal surface. Theoretically, these columns should be free from one of the main disadvantages of OCC (WCOT) with a thin layer of SLP deposited directly on a smooth internal surface, namely the large ratio β of the volumes of the mobile and stationary phases.[3,68,213] This idea was first successfully realised by the application of a static method for depositing porous layers of carriers and active adsorbents from a suspension of these materials in various solvents.[1,3,6,35,68,88,214,215] After the deposition of the porous layer, the internal surface of a metallic capillary (d_c = 0.5 mm) was increased by a factor of 130.[214,215] This led to a decrease in the value of β from 208 to 35.5 with preservation of the HETP characteristic of the original capillary covered with a uniform SLP film with a thickness $d_f \simeq 0.6$ μm. A similar method of preparing CC has been used in other studies.[1,3,88,179] In addition to the static method, use is also made of a dynamic method, which is more suitable for glass CC.[1,3,6,88,216]

Two main types of OCC can be distinguished, depending on the nature of the porous material used: with a porous layer (OCC-PL, or SCOT) and with a solid carrier or adsorbent (OCC-SC, or PLOT).[1,6,68,73,88,113,216–222] The OCC-PL columns used in gas–liquid chromatography are prepared in two ways: a, by depositing a solid carrier previously impregnated with SLP; and b, by the preliminary deposition of a carrier and its subsequent impregnation with the SLP. The thickness of the porous layer in CC of this type is 1–5 μm.[88] In contrast to OCC-PL columns, OCC-SC columns with internal walls carrying a porous layer with a thickness of 10 μm or more, deposited or obtained by chemical methods, are most frequently used in gas-adsorption chromatography.[1,3,6,88,113,215,222] If a porous layer obtained by chemical methods is wetted with an SLP, $d_f > 1$ μm. It is often difficult to draw a line between OCC-PL columns containing an SLP and OCC columns of the WCOT type, obtained by depositing an SLP on an internal surface modified by various methods.[1,3,6,68,88]

OCC-PL columns are prepared using finely divided diatomite carriers,[1,3,6,88,179,214,216] or a mixture of celite with LiCl [223] or with glass.[224] The porous layers may occupy up to 42% of the transverse cross-section of the CC, leading to an increase in the quantity of SLP in the column and hence in the capacity coefficient k' by a factor of more than 100.[3,179] This makes it possible to increase considerably the volume of the specimen introduced, without the danger of overloading the CC.

The properties of OCC-PL columns are intermediate between those of ordinary packed columns and CC with an SLP deposited on the internal walls.[178] Thus in the separation of the methyl stearate–methyl oleate pair (α = 1.12) the values of R_s for a packed column (2.4 m × 2.2 mm), a column with an SLP on the internal wall (WCOT) (46 m × 0.25 mm), and an OCC-PL column (15.2 m × 0.5 mm) were 1.54, 7.06, and 4.09 respectively for analysis times of 35.6, 51.7, and 23.0 min. Increase in the carrier-gas velocity in the capillary columns to values at which R_s = 1.54, as in the case of the packed column, decreased the analysis time to 3.25 min on the OCC-PL column, and to 2.46 min on the WCOT capillary column. Short OCC-PL columns have been used extremely successfully for the rapid analysis of complex organic mixtures, where the times taken for the determination are measured in seconds and tens of seconds.[70,225,226]

OCC-PL columns, while retaining all the main advantages of ordinary packed columns (high capacity, relative short analysis time, stability of operation for a long time) and WCOT capillary columns (high efficiency of separation, possibility of achieving rapid analysis using short CC), show a high stability, durability and reproducibility of the results of qualitative and quantitative analysis.[1,3,6,88] Despite the major achievements of CGC associated with the extensive use of glass and more particularly quartz CC with the most varied

diameters, and also the use of SLP of new types, the importance of OCC-PL columns has not decreased in recent years.[5,68] This is indicated by the fact that one of the leading firms, namely Perkin–Elmer (USA), is continuing up to the present (since 1964) to produce columns of this type.[88]

OCC-SC (PLOT) columns, used in gas-adsorption CGC, have a fairly high capacity and selectivity even in the analysis of low-boiling substances with extremely similar physicochemical properties.[3,5,35,113,180–190,222,227–229] They are therefore widely used to separate isotopes and spin isomers of hydrogen.[227,228] The extensive possibilities provided by capillary gas-adsorption chromatography are indicated, in particular, by the separation at 190 °C of six isotopically substituted methanes on a glass CC (47 m × 0.2 mm) treated with sodium hydroxide.[190] A mixture of gases (He, Ne, Ar, O_2, N_2, and CH_4) was completely separated in 10 min using a 25-metre CC containing as porous layer a thin film of molecular sieves (5 Å).[229] OCC-SC columns have also been used for the successful separation of multicomponent mixtures of hydrocarbons (including C_9), present in natural gases,[3,5,35,113,180,229] and also higher-boiling compounds.[35,181–186,222] In particular, an OCC-SC column (50 m × 0.32 mm) containing as sorbent a mixture of Al_2O_3 and KCl has been used for the successful separation of hydrocarbons up to n-C_{10} and some of their halogen derivatives.[222]

The undoubted advantages of high-capacity OCC-SC columns, namely their high stability, practically unlimited thermal stability, the absence of complications associated with the volatilisation and degradation of SLP, and the fairly high separating power, guarantee a promising future for columns of this type. New methods for preparing OCC-SC columns have much in common with the methods used to prepare OCC-PL columns.[88] CC with high-capacity porous layers with a thickness of 100 μm or more are most frequently prepared by drawing capillaries from tubes containing the adsorbent or carrier.[1,3,88]

c. CC containing colloidal SLP

CC containing colloidal SLP can also be regarded as a form of OCC-SC.[6,84,122,208,209,230–235] Columns of this type are obtained by depositing under static and dynamic conditions a previously stabilised suspension of micro-particles of an active adsorbent with dimensions of $10^{-5}-10^{-7}$ cm in a solution of an SLP which acts as the dispersion medium.[6] Various inorganic substances are used as dispersion phases, including silanised silicas (Silanox),[6,84,230–232,235] highly dispersed silica adsorbents (Aerosil),[208,209] carbon blacks, and zeolites.[3,6,88,122,236,237] The advantages of CC containing colloidal SLP include the possibility of varying their selectivity over a wide range (from the selectivity of the pure SLP forming the dispersion medium to the selectivity of the active adsorbent used as the dispersion phase), the much higher thermal stability of colloidal SLP compared with ordinary SLP, and the universal nature of these columns.[209] Moreover, the use of colloids ensures a higher reproducibility of the adsorption properties of the sorbent compared with SLP modified by small quantities of additives, since in the colloidal deposition, the particles of the dispersion phase are covered with a macro-layer of the SLP.[122] This achieves reproducibility of the retention parameters of the sorbates. While having the same efficiency, CC with colloidal SLP, as a result of their high sorptive capacity, show better separating power than columns on which the stationary phase is deposited from the individual liquid.[208,237]

d. CC with a thick layer of SLP

There is a simple relationship between the extraction coefficient k' and the thickness d_f of the SLP film in WCOT capillary columns; from Eqn. (5) it follows that

$$k' = 4K_L d_f/d_c. \qquad (6)$$

Eqn. (6) indicates one of the most radical methods of increasing the sorptive capacity of these CC, namely by increasing the thickness of the SLP film uniformly deposited on their internal surface. This method became possible as a result of: 1, the introduction into CGC of flexible quartz CC with an internal diameter d_c = 0.32 mm and 0.53 mm, and also glass CC with d_c = 0.75 mm[42,107,113,194,238] and d_c = 0.85 mm;[239] 2, the development of effective methods for treating the internal surface of glass and quartz CC to improve its wettability, making it possible to achieve d_f = 1–8 μm;[42,192,194,197,203,205,240] and 3, the development of varied methods for preparing CC with chemically grafted and transverse cross-linked (immobilised) SLP.[35,42,68,80,88,102,105,109,191,192,194,197,203–205,240–250]

Until early 1983, the thickness of the SLP film in quartz CC with an internal diameter of 0.25 mm and 0.32 mm did not usually exceed 1 μm (as a rule d_f amounted to 0.1–0.5 μm). This made it possible to introduce into CC about 400 ng of any component of a mixture being analysed, without the danger of appreciable overloading.[194] The use of CC with thick SLP films (d_f = 1–8 μm) made it possible to increase several fold the volume of the specimens introduced and to determine the concentration of traces without lowering the efficiency of separation of the components of complex mixtures. Thus when quartz CC (50 m × 0.32 mm) with a methylsilicone immobilised SLP (d_f = 5 μm) was used, increase in the volume of a petrol specimen from 6.5 μg to 130 μg had practically no influence on the separation of the components (the splitting ratio of the stream of carrier gas was 1:10, and the specimen was introduced directly into the CC[107]). In the same work, in an analysis of the middle fraction of hydrocarbons extracted from coal, it was possible to increase the size of the specimen introduced into the CC to 758 μg. Analysis of Eqn. (3) shows that it is appropriate to use CC of large diameter (d_c = 0.53 mm), characterised by high values of k', when the specimen contains pairs of light components difficult to separate.[194] Thus to achieve a degree of separation R_s = 1.5 for a pair of components with α = 1.05 on a CC having a film thickness d_f = 1 μm (k' = 1.9), it is necessary that the number of theoretical plates (n_{req}) be 37120, whereas for a five-fold increase in d_f (k' = 9.6), n_{req} = 19356 t.p. At the same time the ratio of the phase volumes changes from 132 to 26. According to Grob and Grob,[42] an increase in d_f for elastomeric silicone SLP in quartz CC (d_c = 0.32 mm) at the optimum carrier-gas (nitrogen) velocity leads to practically no decrease in the efficiency of separation.

e. The use of immobilised SLP

CC of large diameter (d_c = 0.32, 0.53, and 0.75 mm) with immobilised SLP, operating under isothermal conditions or with temperature programming, are used for the analysis of natural,[113,194,229] petroleum, and fuel gases,[42,107] petrols,[42,194,198,238] mixtures of heavier hydrocarbons,[194,198,239] mixtures of aliphatic acids,[194] pesticides,[194] alcohols,[194] phenols,[194] amines,[201] and various medicinal products.[107,194]

Of particular interest is the use of high-capacity CC with ordinary and chemically cross-linked SLP for the analysis of mixtures of low-boiling compounds having low values of the distribution constant K_L.[42,113,192–194,198,229,238,251] This follows from an analysis of the factor $f(k') = k'/(k' + 1)$ in Eqn. (3). Thus for large values of k', when $k' \simeq k' + 1$, the function $f(k')$ approaches 1 asymptotically with increase in k', and can be regarded as a constant. At low values of k', increase in k' leads to an increase in the function $f(k')$, and hence to an increase in the separation criterion R_s.

The use of a quartz CC (50 m × 0.32 mm) with an immobilised OV-1 methylsilicone SLP (d_f = 1.5 μm) made it possible, with temperature programming, to achieve the practically complete separation of complex mixtures containing saturated, alkene, diene, and acetylene hydrocarbons, formed by the thermal and catalytic transformation of hydrocarbon raw materials.[238]

In addition to the main advantages of CC of large diameter (d_c = 0.53 mm and 0.75 mm) with thick films of immobilised SLP, namely the achievement of high values of the capacity coefficient k',[239,252–254] these columns have a number of other advantages, leading to their extensive application. These advantages are the following: 1, the possibility of introducing the specimen directly into the CC[107,113,194,254] and using other techniques for introducing the specimen without splitting the stream of carrier gas;[239,252,254] 2, the possibility of using CC with an immobilised SLP not only with a flame-ionisation detector but also with other detectors, including a katharometer, a mass spectrometer, and a detector based on Fourier transform infrared spectroscopy;[107,113,194,254] 3, the absence of any need for an additional supply of carrier gas to the detector;[239,254] 4, the possibility of setting up these CC in the thermostat of a chromatograph designed for ordinary packed columns;[107,113,254] 5, the high efficiency of separation (like that of CC of small diameter 0.2–0.25 mm);[107,113,254] 6, a high upper temperature limit for the use of SLP (300–325 °C) with minimum drift of the zero line;[193,239] 7, rapid determination (as when packed columns are used);[252–254] 8, good reproducibility of the specified properties and operational characteristics of the CC during their preparation;[194] 9, the possibility of removing from the CC by means of various solvents the non-volatile components and SLP particles which have not undergone chemical cross-linking, while preserving a high efficiency of separation;[113,194,240] 10, the resistance of the film of immobilised SLP to extraction and elution under the influence of solvents and large specimens of mixtures being analysed;[113,194,240] 11, high stability, which is preserved practically without limit;[113,194,240] 12, a significant decrease in the relative contribution of adsorption effects to the total retention of the sorbates;[254] 13, low catalytic activity, which makes it possible to analyse mixtures containing labile compounds;[239,254] 14, the higher (compared with packed columns) efficiency of CC with a thick SLP film under programmed-temperature conditions, due to the appreciably smaller transverse temperature gradient in the CC and hence the less extensive spreading of the chromatographic zones during the separation;[254] and 15, the low inertia of the heating (compared with packed columns) of CC of large diameter in temperature programming in the thermostat of the columns.[254]

Advantages 8–13 increase considerably the reliability of the identification of the components from the retention parameters. Moreover, the stability of the operation of quartz and glass CC with a thick layer of immobilised SLP under high-temperature conditions makes them particularly convenient for the determination of traces of components in complex mixtures of organic compounds, since a low background level is preserved, and, in particular, it is possible to introduce large specimens directly into a column of large diameter (d_c > 0.32 mm) with a small stream splitting ratio or without splitting of the stream of carrier gas.

A significant disadvantage of CC with thick immobilised SLP films is that their efficiency of separation is lower than that of classical open tubular WCOT capillary columns, because of the increased contribution of intra-diffusion spreading and dynamic diffusion to the spreading of the chromatographic bands.[253]

f. CC with a thin film of immobilised SLP

Chemical immobilisation of the SLP is used not only to increase the extraction coefficient k' of the components but also to increase the selectivity of separation of high-boiling polar and adsorption-active compounds, and also non-polar high-boiling isomers with extremely similar physicochemical properties.[105,108–110,200,203–205,242–250] For this purpose, use is generally made of CC with a diameter of 0.20–0.32 mm with a thin SLP film ($d \leqslant 0.5$ μm), which simultaneously leads to an increase in the efficiency of separation.[105,108–110,200,201,203–205,242–250] Columns of small diameter with a thin film of immobilised SLP retain many of the above-mentioned advantages (5–11, 14, and 15) characteristic of analogous CC of large diameter. On a CC of length 25 m (d_c = 0.20–0.22 mm) with immobilised silicone (SE-30 and OV-101) SLP under programmed-temperature conditions it was possible to achieve the complete separation of fifteen PAH from naphthalene to benz[*g*,*h*,*i*]perylene; C_8, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, and C_{24} n-alkanes and squalane were added to the mixture.[108,109,204] The analysis on glass CC with grafted SLP (OV-1701 methylphenylsiloxane and methylsilicone rubber) of a methylene chloride extract of the particles present in car exhaust gases detected sixteen PAH from phenanthrene to coronene.[250] The high selectivity of immobilised SLP is indicated by the fact that it has been possible, on a CC with a length of not more than 25 m, under programmed-temperature conditions, to achieve the separation of compounds difficult to separate, such as alkyl- and arylcycloalkylphenols (SLP OV-101 and SKTFT-50) and the diastereoisomers of the isoprene alkanes pristane and phytane (SE-30 SLP) in diesel fuel.[109] Capillary columns with immobilised SLP have been used successfully to separate mixtures of varied polar compounds such as amines,[201] phenols, and alkylanilines,[109,205,249] esters, pyridines, alcohols, and free aliphatic acids,[203,205,249] mixtures of high-boiling petroleum distillation products,[105] perfumery products,[249] and mixtures of chemically unstable compounds used in biology and medicine.[105,250]

Relatively short (14–15 m) glass and quartz CC with a thin film of immobilised SLP (d_f = 0.07–0.1 μm) have been used under programmed-temperature conditions[255] to obtain the distillation curve of heavy fractions of petroleum products containing hydrocarbons up to C_{60}–C_{120} (sometimes up to C_{140}) with boiling points of 615–800 °C. Depending on the SLP, the maximum working temperature of the CC was 350–450 °C, and the analysis time did not exceed 2–2.5 h.

g. The preparation of CC with an immobilised SLP

The variety of methods for the immobilisation of the most varied non-polar and polar SLP is leading to their extensive application in CGC.[88,110,194,200,201,238,240,241,256] Grafted SLP are obtained by the reaction of the functional groups of the liquid phase with the surface

hydroxyl groups of the glass.[240,241] The most widely encountered method of immobilisation is by the transverse cross-linking of polymeric liquid phases, carried out directly in the CC.[42,88,105,108–110,194,201–205,240,242–250,256] The phases immobilised include polyethylene glycols,[113,201,203,205,240] methylsilicone phases (SE-30, SE-52, OV-1, OV-101),[102,108–110,194,200,204,238,255] polysiloxane phases SE-54, SE-31, OV-1701, and OV-225 with a small concentration of vinyl and phenyl groups,[42,197,240] phenyl-containing silicone SLP of the OV-17 type,[194,257] phenyl-substituted silicones,[102] etc. Quartz CC with immobilised SLP of the SKTFT-50 silicone type, with operational characteristics equivalent to those of non-Soviet quartz CC, have been obtained in the Soviet Union.[109] The materials used to initiate the transverse cross-linking include various organic peroxides,[42,108–110,197,200,204,238,240,249,256,257] for example benzoyl, dibenzoyl, dicumyl, and t-butyl peroxides, and also cumene and ethylene oxides,[201] and ozone.[240,258] Increased temperature in the presence of a catalyst,[102,203,205] radioactive irradiation,[240,256] and other methods are also used. SLP based on Carbowax 20M have been prepared by carrying out the chemical reaction between the terminal hydroxyl groups of polyethylene glycol and the NCO groups of 1,6-di-isocyanate in glass CC [(11–14) m × 0.25 mm] in the presence of a catalyst at 110–145 °C for 1–5 h.[203] Films of immobilised SLP based on Carbowax 20M-TPA, FFAP, or OV-351 can be obtained by the thermal treatment of these phases in CC at 145 °C for 5 h in the presence of the catalysts Desmodur L-75 (0.002 M) and DABCO R-8020.[204] The immobilisation of silicones leads not only to a marked increase in the UTL at which the SLP can be used (up to 370 °C), but also to an increase in the selectivity, achieved by the preliminary introduction of phenol groups into the framework of the molecule instead of definite oxygen atoms.[102] The polymer obtained in this way, subsequently subjected to dimethyl-substitution and thermal treatment, is immobilised to the extent of 60%, whereas the cross-linking of dimethylsiloxane polymers takes place to the extent of 10%. The extensive application of CC with SLP differing in their selectivity and other important operational characteristics to solve the most varied analytical problems is to a large extent due to studies carried out in the last six years by the firm of Supelco (USA), which has begun the production of columns of this kind with different diameters (0.25, 0.32, 0.53, and 0.75 mm).[113,259,260]

The use of immobilised and other high-temperature SLP extends considerably the range of analytical problems that can be solved by CGC, and enables the latter to compete successfully with highly efficient liquid and fluid chromatography for the determination of high-boiling compounds. Of considerable interest in this connection, in particular, are the carborane–siloxane SLP, many of which (Dexyl-300GC, Dexyl-400GC, Dexyl-410GC, KBS-2, KBS-3, KBS-2F, and KBS-3F) have an UTL of 450–500 °C.[217] Thus an efficient glass CC containing Dexyl-300 (UTL 350 °C) has been used to achieve the complete separation of isomer pairs, difficult to determine, in a 36-component mixture containing a number of PAH from biphenyl to coronene and dibenz(*a*,*h*)pyrenene.[261] These pairs include phenanthrene and anthracene, benz(*a*)anthracene and chrysene, and benz(*e*)pyrene and benz(*a*)pyrene.

Open tubular glass CC with a solid carrier on the internal walls, impregnated with Dexyl-300, can be used under conditions of linear increase in temperature up to 400 °C.[217–221] These CC have been used to separate mixtures of PAH up to coronene,[218] and also microcrystalline waxes.[221]

h. The use of packing as an effective method of increasing the sorptive capacity and selectivity of CC

The most radical method of increasing the sorptive capacity of CC is by filling them with a packing consisting of either an active adsorbent[1,121–123,262–264] or a solid carrier impregnated with the SLP.[1,122,123,126,262,264] To ensure simultaneously a high efficiency of separation, capillary packed columns (CPC) with internal diameter not exceeding 1 mm are generally used.[1,121–125,262–264] Filling CC with a sorbent leads to a sharp decrease in the value of β compared with open tubular CC, with a corresponding marked increase in the capacity coefficient k'. A 23-component mixture containing air, CO_2, and saturated and unsaturated hydrocarbons up to C_6 (specimen volume 50 μl) has been separated on a steel CPC (3 m × 1 mm) filled with aluminium oxide modified with oleic acid (sorbent particle diameter 0.14–0.25 mm) in 16 min at 40 °C.[263] The range of application of these CPC with d_c = 0.6–1 mm is much wider, however.[262–264] The use of long columns, including glass columns, makes it possible to carry out the rapid gas-chromatographic analysis of complex mixtures of alcohols, steroids, barbiturates, and various impurities in air.[1,262]

As noted above in the examination of the efficiency of separation in CGC, in recent years there has been intensive development in a new direction involving the use of micropacked quartz capillary columns (MPQCC) of small diameter (d_c = 0.15–0.37 mm), filled with fine sorbent granules (5–100 μm).[121–127] Short MPQCC with lengths measured in tens of centimetres combine the advantages of open tubular CC and packed columns in relation to their efficiency, capacity, selectivity, and reproducibility of the results of qualitative and quantitative analysis. This makes it possible to use them for the rapid analysis of not only complex mixtures of hydrocarbons[121,123] but also mixtures of strongly polar compounds such as ketones[122,126] and aliphatic and aromatic alcohols.[123]

CPC in general, and MPQCC in particular, have a number of advantages over open tubular CC of the WCOT type.[1,124,126,127,262,263] These advantages, which are a consequence of the high capacity of these CC, are: 1, the possibility of adding the specimen directly to the CC and avoiding splitting of the carrier-gas stream, which decreases the uncertainty in quantitative determinations and lowers the requirements to be satisfied by the sensitivity of the detector (micro-katharometer, mass spectrometer, etc.); 2, the possibility of determining traces; 3, the possibility of separating substances which are weakly sorbed; and 4, the possibility of the micro-preparative separation of extremely narrow fractions of a complex mixture for their subsequent more detailed study by gas-chromatographic and other physicochemical methods. Other advantages of CPC are their practically unlimited thermal stability and their stability of operation when filled with adsorbents, and the much less severe requirements to be satisfied by the solid carrier and the SLP, compared with OCC-PL and columns in which a phase is deposited directly on the internal surface.

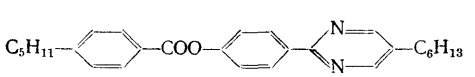
Nevertheless, the extensive use of these columns is limited by the complexity and time-consuming nature of the procedure for filling CPC (and more particularly MPQCC) and by the high pressure drops established during use, which in a number of cases reach several MPa.[122]

i. The use of liquid-crystalline SLP

The use of nematic liquid-crystalline SLP in CGC is directed mainly to increasing the selectivity of separation of isomeric

compounds with extremely similar boiling points and other physicochemical properties.[7,35,39–41,66,89,122,176,195,196,237,265–269] The high selectivity of liquid crystals in the nematic state is due to the long-range orientational order of the arrangement of the long axes of their molecules. The use of these SLP combined with highly effective CC makes it possible to solve the most complex analytical problems, including the separation of stereoisomers. The possibility of separating C_8 arenes and isopropylbenzene on a 50-metre CC containing *p,p'*-azoxyphenol (AOP) and *p,p'*-methoxyethoxyazoxybenzene (MEAB) has been studied.[268] A more detailed study of the *meta–para* selectivity of liquid-crystalline SLP and their mixtures in the temperature range 90–160 °C in copper CC (40 m × 0.35 mm) showed that the maximum selectivity is achieved with the maximum steric effect in the liquid-crystalline melt.[195] An interesting feature is that in the temperature range of existence of the nematic liquid-crystalline state, the more linear isomer *p*-xylene is retained more strongly than *m*-xylene, distinguishing these SLP from most other SLP which are not liquid crystals.[195,237,268] The influence of temperature on the efficiency of separation, the separation factor α, and the capacity coefficient k' in CC with liquid-crystalline phases is much more complex than in the case of SLP in which there is only short-range translational order. This is related both to the change in the state of aggregation of the SLP on passing through the melting point and to the change in the phase state of the liquid phase with increase in temperature (the change from the smectic to the nematic and then to the isotropic state).[89,195,237] In general, the temperature of maximum selectivity does not necessarily coincide with the temperature of the maximum capacity.[195] The optimum separation temperature may not coincide with the temperature of maximum retention in the range of the meso-phase.[195]

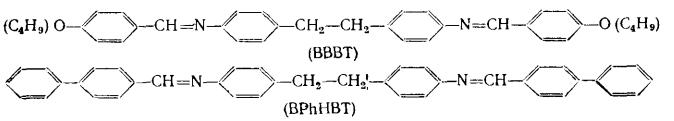
The use of sodium glass capillary columns (d_c = 0.23 mm) of different length containing the new liquid-crystalline SLP 2-[4-(4-pentylbenzoyloxy)phenyl]-5-hexylpyrimidine (PBHP)



(PBHP)

in the temperature range 80–130 °C has been used to separate a complex 32-component mixture consisting of C_8–C_{13} n-alkanes and C_8–C_{13} alkylbenzenes.[66] The specific efficiency of the CC used was 3500 t.p. m^{-1}, the capacity coefficient k' = 3.5 (at 90 °C), and d_f = 0.115 μm. A remarkable feature is that despite the fact that the SLP used by the authors cited[66] had a higher selectivity with respect to *p*- and *m*-xylenes than all known liquid-crystalline SLP ($\alpha^{100\ °C}$ = 1.09, $\alpha^{50\ °C}$ = 1.13, $\alpha^{25\ °C}$ = 1.20), it was not possible to separate all the components of the mixture studied on a single column of length 50 m. An extremely satisfactory separation in a relatively short time (~20 min) at 25 °C was achieved only using a combined CC, the first section of which, of length 35 m, contained OV-101 methylsiloxane rubber as SLP, while the second, of length 15 m, contained PBHP. The temperature range corresponding to the nematic liquid-crystalline state of PBHP is 38–159 °C.

Interesting studies have been carried out on the separation of PAH.[89,196] In particular, a CC with the liquid-crystalline SLP N,N'-bis-4-butoxybenzylidene-*a,a'*-bi-*p*-toluidine [N,N'-bis-(BaBT)] has been used for the complete separation of benz(*a*)anthracene and chrysene.[196] The complete separation of a number of tricyclic, tetracyclic, and pentacyclic PAH and two benzofluoranthenes has been carried out using glass CC containing the liquid-crystalline SLP



(BBBT)

(BPhHBT)

whose nematic phase is thermodynamically stable at relatively high temperatures (188–300 °C for BBBT).[89] To increase the UTL and the stability of operation of the CC at high temperatures, the BPhHBT and BBBT were deposited on a previously treated surface carrying $BaCO_3$ crystals. The further development of this promising field is restricted at present by the non-availability of liquid crystals having sufficient thermal stability and undergoing phase transitions in the range 300–350 °C, so that it is not possible to cover all the PAH present in the specimens in the analysis of petroleum products and environmental specimens. Difficulties arise as a result of the instability of the separating power of liquid crystals, which leads to a sharp deterioration in the efficiency of the CC during use, particularly under temperature-programming conditions at high temperatures. When combined with highly efficient liquid chromatography, however, the use of CC containing liquid-crystalline SLP provides unique analytical possibilities for determining PAH in various technical and natural materials. As noted above, the separating power of CC containing liquid-crystalline SLP can be increased considerably by the action of an electric field.[176]

Interesting results have been obtained[39] using a quartz CC with a liquid-crystalline SLP to separate isomeric polycyclic aromatic compounds whose molecules contain different heteroatoms. Quartz CC (15 m × 0.20 mm) containing a nematic polysiloxane SLP have been used to separate PAH with relative molecular masses of 276–302 at 280 °C, and quartz CC (25 m × 0.20 mm) with a smectic polysiloxane SLP have been used to separate the methyl esters of aliphatic acids at 140 °C.[40] The unique selectivity of liquid-crystalline SLP is indicated by the results of studies[41] in which a glass CC was used to separate a number of geometric isomers of various polar and non-polar compounds.

Additional possibilities for the rapid determination of various hydrocarbons, aliphatic acids, esters, and nitriles are provided by the use of short CC (up to 10 m) containing colloidal liquid-crystalline SLP.[237]

j. The influence of adsorption effects

An important factor controlling the selectivity and capacity in CGC is the adsorption of the sorbates at the inter-phase surfaces in CC in which their internal surface plays the part of the solid carrier.[75,122,269,270] It has been shown convincingly[122,270–273] that the additive theory of retention is equally applicable to capillary and packed columns. The important part played by adsorption phenomena in CGC is indicated primarily by the dependence of the retention indices of a number of compounds, including even low-boiling C_6–C_7 hydrocarbons, on the nature of the surface of the walls of the capillary and the thickness of the SLP film.[122,169,269–274] The factors indicated have a significant influence on the retention of compounds in chromatography using both polar and non-polar SLP. A change in selectivity has been observed with increase in the effective thickness of the film of a liquid-crystalline SLP.[269] The influence of the thickness of the layer of SLP on retention has been observed for CC of practically all types.[122,169,270] An extremely important practical feature is that in some cases a change in the

concentration of the SLP in the CC even changes the order of elution of the compounds being determined. For example, in a glass CC containing Carbowax 20 M (k' = 2.1 for *cis*-pentadec-5-ene), *trans*-pentadec-6-ene is eluted first, followed by *cis*-pentadec-5-ene, whereas in a CC with a thin layer of the same SLP (k' = 1.3), the opposite order of elution is observed.[270,271]

k. The use of mixed SLP

Despite the high specific efficiency of CC, in particular quartz CC, the use of mixed SLP to carry out complex separations in single-column CGC is still of considerable interest, since it makes it possible to control the capacity and selectivity factors over wide limits and to some extent to avoid the successive use of several individual SLP.[86,174,206,207,275] The smooth control of the polarity of the stationary phase by the simultaneous deposition of two readily available individual SLP in definite proportions is appropriate for separating extremely complex organic mixtures consisting of substances of different classes which differ in the polarity of the molecules to be separated.[206] Here, the polarity of molecules is understood to mean not the empirical value of their dipole moment but a quantity determined by the concentration of polar functional groups or by the ratio of the polar and non-polar atomic groups in the sorbate molecule.

Glass (d_c = 0.45 mm) and quartz (d_c = 0.22 mm and 0.33 mm) CC with binary SLP containing Superox 20M† (polar component) and OV-1 (non-polar component) in different proportions (1:3, 1:1, and 3:1) have been used to separate synthetic mixtures containing alcohols, aliphatic acids, diols, phenols, anilines, primary and secondary amines, and the components of vegetable oil from hops with the addition of various aromatic substances.[68] It has been shown that by varying the composition of this mixed SLP over a wide range it is possible to cover a wide range of McReynolds constants, characteristic of five individual SLP of the Yukon type. An important result of the work cited[86] is that it proved that it is possible to deposit, on the untreated internal surface of a CC, films of mixed SLP capable of stable functioning up to 250 °C, in spite of the fact that one of its components (Superox 20M) tends to form droplets, and the UTL of each of the individual SLP does not exceed 170–180 °C. The formation of stable films of mixed SLP on a smooth fused quartz surface which has not been treated to give it roughness has made it possible to make full use of the advantages of quartz CC, which have low adsorption and catalytic activity, and at the same time to achieve a high efficiency of separation.

A number of mixtures of PAH have been analysed in CC with liquid-crystalline SLP of the N,N'-bis-(BaBT) type, mixed with OV-101 polysiloxane, and the optimum ratio of the polysiloxane and the liquid-crystalline components of the SLP has been determined.[207]

The use of CC with mixed SLP previously made possible the detailed determination of the light hydrocarbons present in petrol fractions.[158,170,276–278] In particular, a CC with a mixed SLP was used under programmed-temperature conditions to obtain detailed information on the composition of a broad C_4–C_{12} petrol fraction.[170] CC with a mixed SLP have been used to separate aromatic C_6–C_{10} hydrocarbons.[277,278]

The use of mixed SLP often makes it possible to pass smoothly through the entire range of polarity. The optimum composition of the binary SLP and the length of the CC are usually calculated from the required degree of separation of the components of the mixture being analysed and the minimum analysis time. The most convenient for this purpose is the method of "window" diagrams,[279] subsequently extended to the selection of the optimum experimental conditions for the use of combined columns (connected in series).[66,275,280–282] In this method, the linear dependence of the coefficient k' on the composition of the mixed SLP is constructed for each component of the mixture being analysed. From these relationships, for any specified composition of the SLP, it is possible to calculate the selectivity coefficient α for pairs of components most difficult to separate. The plot of α against the SLP composition, called the "windows" diagram, makes it possible to select the optimum composition of the binary SLP corresponding to the maximum value of α. The length of the CC required for the separation is selected from the number of theoretical plates (n_{req}) required for the complete separation of the components.

Despite their obvious advantages, the extensive use of mixed SLP in CGC is associated with a number of difficulties, including the following: 1, the limited mutual solubility of the polar and non-polar components of the SLP, which in a number of cases leads to the adsorption of the sorbates on a new inter-phase boundary which is difficult to take into acocunt, and the possibility of varying the capacity and selectivity factors only in a relatively narrow range;[275] 2, the deterioration in the efficiency of separation and the poor reproducibility of the properties of the CC as a consequence of the insufficient wettability of their internal surface by the mixed SLP;[275] and 3, the need in a number of cases for the successive application of CC containing mixed SLP with different compositions to obtain the required volume of information.

IV. Summary

The examination of a large number of methods for controlling efficiency, selectivity, and capacity in single-column CGC indicates the significant achievements and the promising possibilities of this most widely encountered and flexible method for the analysis of multicomponent mixtures of organic and inorganic compounds. At the same time there are obvious limitations and difficulties associated with use of CGC to solve various complex analytical problems, which cannot always be overcome using gas-chromatographic systems with one CC. This applies primarily to the analysis of natural and other mixtures boiling over a wide temperature range and consisting of representatives of varied classes of chemical compound. The separation of these mixtures often becomes possible only after the preliminary isolation of the fractions to be analysed, which unavoidably leads to distortion of the initial composition of the specimens being studied and is also time-consuming. In a number of cases, to obtain detailed data on the concentration of the individual components in specimens characterised by a wide variation in composition, it is necessary to carry out parallel or successive analyses using several instruments, sometimes under different temperature conditions and using CC with SLP having different polarity. The frequent replacement and alternation of CC having different efficiencies, selectivities, and capacities, and analyses using different chromatographs, are also time-consuming and inconvenient, and lead to an increase in the number of sources of error in the determination of the composition of complex mixtures.

Difficulties frequently arise, associated with the need to carry out analyses at a low temperature or, on the other hand, a temperature

† Superox 20 M is a linear polyethylene glycol with a relative molecular mass of 20000–40000, readily soluble in dichloromethane.

which is too high, with large pressure drops, when using long CC and CC of other types characterised by a high specific resistance to the flow of carrier gas (CC with a diameter reaching 0.1 mm, MPQCC, etc.). Change in the temperature of the CC and the use of temperature programming in the analyses are not always effective in the study of complex mixtures, since improvement in the separation of some pairs of compound may be accompanied by a deterioration in the separation of other pairs. Moreover, the use of high temperatures, even for a short time interval, leads to the danger of decomposition of the substances being analysed, to a decrease in the lifetime of the CC, and to the incomplete realisation of their potential efficiency.

Although glass and more particularly quartz CC with ordinary and immobilised SLP have good operational characteristics, their use in large-scale analyses requires highly qualified workers. Many types of CC and SLP are difficult to obtain, in short supply, and expensive. Certain difficulties are associated with the procedures preceding the deposition of SLP on the internal surfaces of CC and carried out to eliminate or decrease its adsorption and catalytic activity and to improve the wettability of this surface by the liquid phase.

Despite the fact that the chromatographic characteristics of OCC-PL, OCC-SC, and micropacked glass and quartz CC are highly stable for a long time, and their UTL fairly high, they have not yet been widely applied, because of the difficulty of their preparation.

The extensive use of liquid-crystalline, mixed, and colloidal SLP in CGC is prevented by the changeability of their separating power, particularly at relatively high temperatures, and by the difficulty of achieving reproducibility of the efficiency and selectivity of columns containing these phases.

Extensive possibilities for varying the efficiency of separation over a wide range are provided by two-stage systems with capillary columns functioning under circulation gas-chromatographic conditions.[283–286] Programming the length of the layer of sorbent in the gas-chromatographic process makes it possible, at low carrier-gas inlet pressures, and by the repeated use of each of two CC with the same SLP, to achieve values of the efficiency of separation measured in tens of millions of t.p., which makes it possible to achieve values of the separation factor α extremely close to 1 (1.002 – 1.01) in the separation of isotopically substituted organic compounds with extremely similar properties (cyclohexane, benzene, naphthalene, acetone) and their partly or completely deuteriated analogues.[283–286]

Promising possibilities for the extension of the use of CGC for the analysis of complex mixtures and the reliable determination of micro-quantities are provided by the use of gas-chromatographic systems with several columns, of which at least one is a capillary column.[9–13,16,18,55–64,66,177,275,280–282,287–291] These systems make it possible to obtain extremely detailed information on the composition of the mixture being analysed, since it is possible to vary the capacity and selectivity parameters over an extremely wide range and to carry out the analyses at relatively low temperatures. The last feature guarantees the high stability of the CC for a long time, and extends the range of compounds that can be determined, by including thermally labile and reactive substances. This makes it possible, even with an extremely limited number of CC and SLP and small quantities of the substance being analysed, to decrease the total time taken for the determination and to increase the reliability of the analysis by eliminating undesirable operations of specimen preparation, using relatively short CC, and decreasing the total number of experiments. The use of high-capacity packed columns combined with highly efficient CC provides extensive possibilities for increasing the sensitivity of determinations. By carrying out analyses in multi-stage gas-chromatographic systems containing two or more CC with different SLP and detectors, it is also possible in a number of cases to increase the reliability of the identification of the components of complex mixtures of organic compounds.

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The synthesis and properties of thioaldehydes

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ABSTRACT. Data on the synthesis of thioaldehydes, a little investigated class of organic sulphur compounds, are described systematically and surveyed. Various types of relatively unstable thioaldehydes and thioaldehydes stabilised by electronic and steric factors are examined. Their physical, spectroscopic, and chemical properties are discussed. The important role of thioformyl compounds as intermediates and synthons is demonstrated.

The bibliography includes 92 references.

Contents

I. Introduction 378
II. Thioformaldehyde and thioacetaldehyde 378
III. Alkoxy-, acyl-, and alkoxycarbonyl-thioformaldehydes 379
IV. αβ-Unsaturated and aromatic thioaldehydes 380
V. Sterically stabilised thioaldehydes 387
VI. Physical properties of compounds with the thioaldehyde group 388
VII. Chemical properties of thioformyl compounds 389

I. Introduction

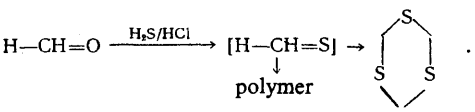
The chemistry of aldehydes has been developing successfully since the beginning of the past century. They are used widely in the synthesis of acetals, oximes, hydrazones, carboxylic acids, amines, alcohols, diols, etc., and in the manufacture of polymers, medicinal preparations and perfumes, dyes, pesticides, explosives, etc.[1] However, their sulphur analogues, thioaldehydes (TA), were ignored for a long time. This was because for historical reasons the view was established that TA are extremely unstable and that their synthesis and study are therefore difficult.

The first communications on stable TA appeared as late as 1960.[2,3] They probably in fact initiated the development of the chemistry of this class of compound. The role of TA as important intermediates and synthons in organic chemistry and also as practically useful substances became increasingly clear from the individual publications which appeared in the second half of the present century. For example, 5-thioformyldipyrrolylmethane has been used as a key compound in the total synthesis of chlorophyll.[3] Penicillins have been converted into biosynthetically important peptides through TA derived from mercaptoazetidinone;[4,5] thioformylmethylene derivatives of heterocyclic bases have begun to be used in the synthesis of photosensitive materials.[3] At the present time, there has been an appreciable growth of interest in TA. Communications about the generation and reactions of thioformaldehyde, thioacetaldehyde (Section II), thioacrolein, and thiobenzaldehyde (Section IV), which previously did not attract attention because of their extreme instability, are being published with increasing frequency. Modern physicochemical methods have made it possible to establish the lifetimes of these compounds, to obtain their spectroscopic characteristics, and to discover their involvement as intermediates in many chemical reactions. A trend has arisen towards the specific synthesis of fairly stable TA stabilised by electronic (Section IV) or steric (Section V) factors associated with substituents. Increasing attention is being devoted to the study of the properties of TA.

The chemistry of TA has been developing mainly abroad and chapters in several reviews in the German language have already been devoted to them,[6–12] but unfortunately they have by no means covered all the available data. The present review is being published because of a wish to draw the attention of Soviet investigators to compounds of this class.

II. Thioformaldehyde and thioacetaldehyde

The simplest representative of TA, thioformaldehyde, is extremely unstable. Its half life is ~6 min at a pressure of 0.01–0.05 Pa.[11] One of the initial (1868) synthetic approaches to thioformaldehyde was based on what has now become the classical reaction of formaldehyde with hydrogen sulphide in the presence of acid catalysts:[6]



The thioformaldehyde reaction products, which are, depending on the reaction conditions, 1,3,5-trithiane (trithioformaldehyde) or polymethylene sulphides, have served as indirect evidence for the primary formation of thioformaldehyde. Subsequently, the successful development of the methods of synthesis of thioformaldehyde in combination with modern physicochemical research methods made it possible to establish unambiguously the possibility of the existence of monomeric thioformaldehyde.[7,8,10] The use of the pulse thermolysis technique, whose undoubted advantages are a very short reaction time (at a reduced pressure) and the possibility of analysing the pyrolysis product in the gas phase, should be regarded as one of the most productive achievements in this field. Monomeric thioformaldehyde has been obtained by the thermolysis of various sulphur compounds, for example thietan, dimethyl disulphide, 1,2,4-trithiolan, and methanesulphenyl chloride.[10,13]

It is very remarkable that thioformaldehyde has been detected in cosmic space.[10] The prolonged existence of such highly reactive molecules in the interstellar vacuum and cold is possible because of the large intermolecular distances. Such conditions in fact ensure the

stability of individual thioformaldehyde molecules, which usually exhibit a high tendency towards oligomerisation and polymerisation.

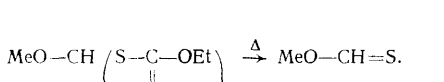
The closest homologue of thioformaldehyde, namely thioacetaldehyde, is also very unstable. In contrast to thioformaldehyde, it can exist in the tautomeric enethiol form (ethenethiol):

$$CH_3{-}CH{=}S \rightleftarrows CH_2{=}CH{-}SH.$$

Thioacetaldehyde is generated in different ways: photochemically by adding hydrogen sulphide to acetylene,[10] by the thermolysis of ethane-1,2-dithiol[10] and dimethyl sulphide,[14] and by the reaction of vinyl chloride with an excess of hydrogen sulphide.[14] On thermal decomposition of 2-vinylthiotetrahydropyran, the isomeric α- and β-trithioacetaldehydes were isolated.[15]

III. Alkoxy-, acyl-, and alkoxycarbonyl-thioformaldehydes

O-Substituted thioformates (RO−CH = S), which can be regarded as alkoxythioformaldehydes, are interesting not only as unusual representatives of thiocarbonyl compounds but also as reagents for the introduction of the thioaldehyde group.[16,17] *O*-Ethyl thioformate was first obtained in 33% yield by the hydrothiolysis of ethyl orthoformate.[18] Later a new, simple, and more effective procedure, starting with the readily available 1,1-dichloromethyl methyl ether, was proposed for the synthesis of *O*-alkyl thioformates using the *O*-methyl derivative as an example.[19] Heating potassium *gem*-bis(*O*-ethyl dithiocarbonate) (I), obtained by the reaction of dichloromethyl methyl ether with *O*-ethyl dithiocarbonate, to 200−220 °C leads to *O*-methyl thioformate. This compound is sensitive to oxygen but can be stored in a nitrogen atmosphere at 0 °C for several months:



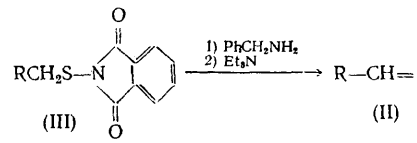
(I)

The attempt to synthesise *O*-phenyl thioformate by a similar procedure led to polymerisation products only.[19]

Acyl- and alkoxycarbonyl-thioformaldehydes (R−CO−CH = S, RO−CO−CH = S) represent a special variety of thiocarbonyl derivatives in which the electron-accepting carbonyl functional group is linked to the CH = S group. Such compounds have not been isolated in the monomeric state. However, their intermediate formation has been used for the synthesis of cyclic adducts.[20–22]

Bunte salts RCH_2SSO_3Na are used for the synthesis of R−CO−CH = S with R = Ph or PhNH[20] (see above), while the corresponding α-sulphonyl disulphide $4\text{-}BrC_6H_4COCH_2SSCH.(SO_2Tol)COC_6H_4Br\text{-}4$ has been used to obtain the thial with R = $4\text{-}BrC_6H_4$[21] (see below). Ph−CO−CH = S can also be obtained by the photolysis of diphenacyl sulphide.[22]

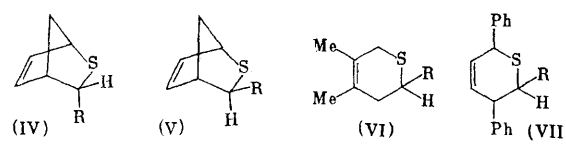
The first information about methoxycarbonylthioformaldehyde (IIa) can be found in the communication by Harpp and Back.[23] In a study of the reaction of *N*-(methoxycarbonylmethylthio)-phthalimide (IIIa) with benzylamine at room temperature, the thioxoamide $PhCH_2NHCOCSNHCH_2Ph$ was isolated. It was then assumed that methoxycarbonylthioformaldehyde (IIa) is an intermediate in this reaction:



(III) (II)

R = MeO−CO (a), EtO−CO (b).

The reactions of compounds (IIIa, b) with triethylamine in the presence of conjugated dienes lead to the corresponding alkoxycarbonylthioformaldehydes (IIa, b) *in situ*.[24] The *endo*-adducts (IV) and the *exo*-adducts (V) of cyclopentadiene and ethoxycarbonylthioformaldehyde (IIb) dissociate at 111 °C, which makes it possible to achieve the transfer of the TA (IIb) to other conjugated dienes. Thus, when a "kinetic mixture" of compounds (IV) and (V) with 2,3-dimethylbuta-1,3-diene was heated in toluene under nitrogen in a sealed tube at 120 °C for 21 h, the individual adduct (VI) was obtained in 82% yield. In the case of *trans,trans*-1,4-diphenylbuta-1,3-diene, which reacts with maleic anhydride 114 times more slowly than 2,3-dimethylbuta-1,3-diene,[25] refluxing of a mixture of the isomers (IV) and (V) in xylene readily affords the adduct (VII) (mixture of stereoisomers). Thus the thermal dissociation of the adducts (IV) and (V) can be used preparatively as the source of ethoxycarbonylthioformaldehyde (IIb):



(IV) (V) (VI) (VII)

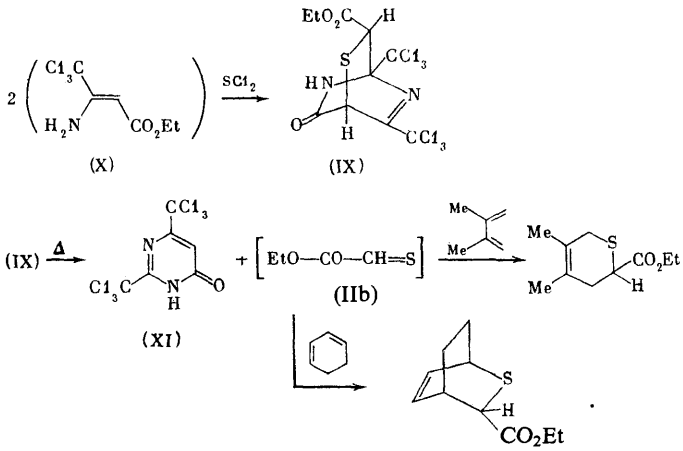
R = EtO—CO.

Bunte salts[20] and α-sulphonyl disulphides[21] are excellent substrates for the synthesis of alkoxycarbonylthioformaldehydes (II) and the acyl derivatives.

The 1,2-elimination of HCl; from ethoxycarbonylmethanesulphenyl chloride (EtO−CO−CH_2SCl) (VIII) when it is treated with triethylamine leads to ethoxycarbonylthioformaldehyde (IIb).[26] It too is trapped by various conjugated dienes. The yield of the products of [2 + 4]cycloaddition is then satisfactory. However, the interaction of the TA (IIb) with cyclohexa-1,3-diene is accompanied by the formation of other reaction products, probably as a result of the competing attack by the sulphenyl chloride (VIII) on the diene.[26]

A derivative of diazathiabicyclooctene (IX) has been recommended as a new precursor of alkoxycarbonylthioformaldehydes (II).[27] Compound (IX) was obtained in 34% yield by the reaction of ethyl 3-amino-4,4,4-trichlorocrotonate (X) with SCl_2. Heating of a solution of compound (IX) in chlorobenzene at 80 °C induces a retro-Diels-Alder reaction and the formation, together with the product (XI), of ethoxycarbonlthioformaldehyde (IIb), which has been successfully trapped with cyclohexa-1,3-diene or 2,3-dimethyl-

buta-1,3-diene (the yields of the adducts were 85% and 48% respectively):



This method of generating and trapping ethoxycarbonylthioformaldehyde (IIb) supplements effectively the recently developed elegant methods of synthesis of thioformyl compounds.[20–22]

The synthesis of n-butoxycarbonylthioformaldehyde from n-butylglyoxal and P_4S_{10} as well as its reactions with dienes have been briefly reported.[26]

IV. αβ-Unstaturated and aromatic thioaldehydes

The methods of synthesis of αβ-unsaturated and aromatic TA are extremely varied. At the present time they can be subdivided into 12 general methods.

1. Thionation of aldehydes

The methods for the direct conversion of the carbonyl group ($>C=O$) into the thiocarbonyl group ($>C=S$)[11] in order to synthesise TA are rarely used. In the synthesis of 3-thioformylindolizines (XII) by the appropriate treatment of the corresponding formyl derivatives, the use of tetraphosphorus decasulphide is by no means as convenient as the employment of other thionating agents[28] (Table 1, Nos. 1–3). P_4S_{10} has been used to synthesise dimethylaminothioacroleine (XIII),[29] but no experimental data have been published.

The interaction of 2-pyrrolidinobenzaldehyde with Lawson's Reagent† in boiling toluene leads initially to the corresponding TA (XIV).[30]

The reactions of boron sulphide with benzaldehyde and its 3-methyl and 3-nitro-derivatives have also been investigated.[31] The 3-nitro-derivatives do not react with P_2S_3, while in the two remaining cases cyclic trimers of the corresponding TA—substituted 1,3,5-trithianes—were isolated. Such trimerisation is apparently promoted by thionation catalysts (HCl, I_2).

† 4-MeOC$_6$H$_4$—P(S)(S)P(S)—C$_6$H$_4$OMe-4

2. Thionation of oximes and hydrazones

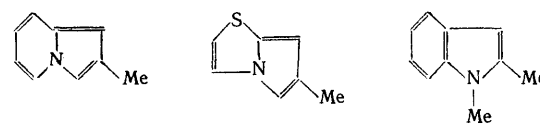
Refluxing of the oxime (XV) or the hydrazone (XVI) of 6-formylpurine in thioacetic acid or its anhydride leads to *N*-acetyl-6-thioformylpurine (XVII)[32] (Table 1, No. 4).

3. Hydrothiolysis of iminium salts

Iminium salts have been used successfully for the synthesis of thioformyl compounds (Table 1, Nos. 5–15).

The first stable thioaldehyde—3-ethyl-4′-methoxycarbonyl-5′-(2-methoxycarbonylpropionyl)-3′, 4-dimethyl-5-thioformyldipyrrolylmethane (XVIII)—was obtained by Woodward et al.[2] by the reaction of *N*-ethylformiminium bromide (XIX) with hydrogen sulphide in the presence of sodium methoxide in a benzene–methanol mixture. Slightly later, the enaminothial (XXI) was synthesised in a satisfactory yield by the reaction of a 1-ethyl-2-(2-*N*-methyl-*N*-phenylaminoethenyl)benzothiazolium salt (XX) with sodium hydrogen sulphide in methanol.[3]

A brief communication appeared in 1966[33] in which the problem of the synthesis of stable TA from 2-methylindolizine (XXII), 6-methylpryolo[2,1-*b*]thiazole (XXIII), and 1,2-dimethylindole (XXIV) was posed for the first time. It was correctly suggested that coupling of the thioformyl group to a nitrogen atom in a heterocycle can lead to the mesomeric stabilisation of the corresponding TA, for the synthesis of which a new version of the Vilsmeier–Haack reaction was used:[33]



(XXII) (XXIII) (XXIV)

Treatment of the initial compounds (XXII)–(XXIV) in dimethylformamide (DMF) with phosphoryl chloride leads to the Vilsmeier salts (XXV)–(XXVII) respectively, whose solvolysis *in situ* by aqueous sodium hydrogen sulphide affords the orange or red TA (XIIb), (XXVIIIa), and (XXIX).

Later the thioformylindolizines (XII) and (XXX)[28] and thioformylpyrrolo-[2,1-*b*]thiazoles (XXVIII) and (XXXI)[34] were synthesised by the same procedure and investigated in detail. The electrophilic substitution reactions in indolizines occur preferentially at the 3-position or, if the latter is occupied, to the 1-position. 3-Thioformyl-substituted compounds (XIIa, b, d–g) have been obtained in excellent yields from indolizine, 2-methylindolizine, and 1,2-, 2,6-, 2,7-, and 2,8-dimethylindolizines. 2-t-Butylindolizine gives rise to 5% of 1-thioformylindolizine (XXXa) together with the 3-formyl-substituted derivative (XIIc). The attempts to obtain the 1,3-dithioformyl derivative (XIIh)[28] led only to a polymer. Under these conditions, the two thioformyl groups were probably mutually destabilised as a result of cross-coupling.

A modified Vilsmeier reaction made it possible to synthesise a large series of thioformyl-substituted 5- and 7-pyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI).[34] A 4:1 mixture of the 5-thioformyl derivative (XXVIIIe) and the 7-thioformyl derivative (XXXIe) has been obtained from 3,6-dimethylpyrrolo[2,1-*b*]thiazole. 6-t-Butyl-3-methylpyrrolo[2,1-*b*]thiazole also affords a mixture from which the 5-thioformyl derivative (XXVIIId) and the 7-thioformyl derivative (XXXId) were isolated by preparative thin-layer chromatography (TLC). The structure of the 5-thioformyl derivative (XXVIIId) was reliably confirmed by X-ray diffraction.[34]

Table 1. αβ-Unsaturated, aromatic, and sterically stabilised thioaldehydes.

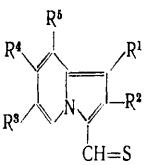
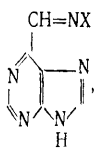
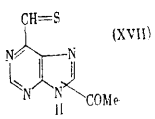
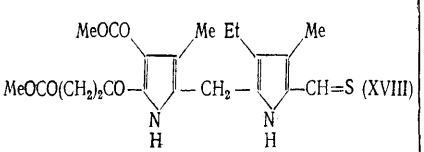
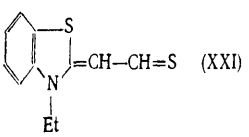
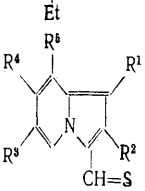
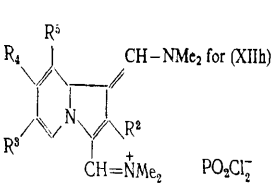
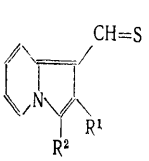
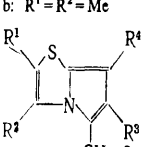
No.	Reagents	R–CH=S	M.p., °C	Yield, %	Refs.
1	R–CH=O, P_4S_{10}	 (XII)			
		c = $R^1=R^3=R^4=R^5=H$, $R^2=Me$	88–89	59	[28]
		d = $R^3=R^4=R^5=H$, $R^1=R^2=Me$	168–169	76	[28]
2	R–CH=O, P_4S_{10}	$Me_2NCH=CH-CH=S$ (XIII)	61–63	—	[29]
3	R–CH=O, Lawson reagent	2-[$N(CH_2)_4$]–C_6H_4–CH=S (XIV)	—	—	[30]
4	 MeCOSH or $(MeCO)_2S$	 (XVII)			
	(XV): X=OH		182–184	28	[32]
	(XVI): X=NH_2		—	34	[32]
5	R–CH=$\overset{+}{N}$HEt Br^-, H_2S (XIX)	 (XVIII)	145–146	—	[2]
6	R=CH–CH=$\overset{+}{N}$(Me)Ph X^-, NaSH (XX)	 (XXI)	—	—	[3]
7	R–CH=$\overset{+}{N}Me_2PO_2Cl_2^-$, NaSH (XXV)	 (XII)			
		a: $R^1=R^2=R^3=R^4=R^5=H$	56.5–58	77	[28]
		b: $R^1=R^3=R^4=R^5=H$, $R^2=Me$	88–89	86	[28]
		c: $R^1=R^3=R^4=R^5=H$, $R^2=t$-Bu	139–141	90	[28]
		d: $R^3=R^4=R^5=H$, $R^1=R^2=Me$	168–169	81	[28]
		e: $R^1=R^4=R_5=H$, $R^2=R^3=Me$	150–152	86	[28]
		f: $R^1=R^3=R^5=H$, $R^2=R^4=Me$	140–142	83	[28]
		g: $R^1=R^3=R^4=H$, $R^2=R^5=Me$	167–170 (decomp.)	82	[28]
	 for (XIIh)	h: $R^3=R^4=R^5=H$, $R^2=Me$, $R^1=CH=S$	197–200 (polymer)	96	[28]
8	R–CH=$\overset{+}{N}Me_2$ $PO_2Cl_2^-$, NaSH (XXV′)	 (XXX)			
		a: $R^2=H$, $R^1=t$-Bu	129–131	5	[28]
		b: $R^1=R^2=Me$	158.5–159	76	[28]
9	R–CH=$\overset{+}{N}Me_2$ $PO_2Cl_2^-$, NaSH (XXVI)	 (XXVIII)			

Table 1 (contd)

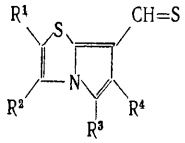
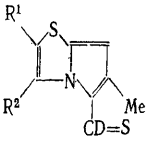
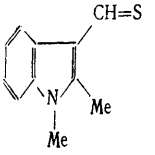
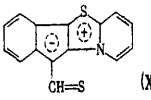
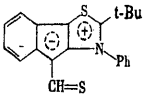
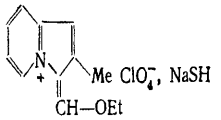
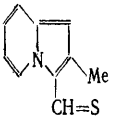
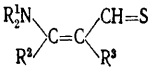
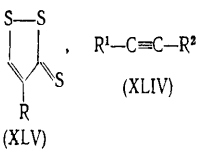
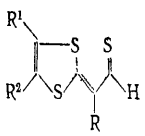
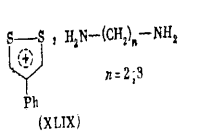
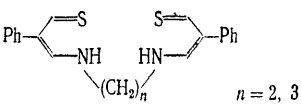
No.	Reagents	R—CH=S	M.p., °C	Yield, %	Refs.
		a: $R^1=R^2=R^4=H$, $R^3=Me$	101—103	89	[34]
		b: $R^2=R^4=H$, $R^1=R^3=Me$	127—128	89	[34]
		c: $R^1=R^2=H$, $R^3=R^4=Me$	165—165.5	71	[34]
		d: $R^1=R^4=H$, $R^2=Me$, $R^3=t$-Bu	117—118	12	[34]
		e: $R^1=R^4=H$, $R^2=R^3=Me$	152—154	49	[34]
		f: $R^4=H$, $R^1=R^2=R^3=Me$	169—170	77	[34]
10	R—CH=$\overset{+}{N}$Me$_2$ $PO_2Cl_2^-$, NaSH (XXVI′)	 (XXXI)			
		a: $R^1=R^2=H$, $R^3=R^4=Me$	162.5—164.5	65	[34]
		b: $R^1=H$, $R^2=R^3=R^4=Me$	195—199	92	[34]
		c: $R^1=R^2=R^3=R^4=Me$	224—226 (decomp.)	75	[34]
		d: $R^1=R^3=H$, $R^2=Me$, $R^4=t$-Bu	156—158	17	[34]
		e: $R^1=R^3=H$, $R^2=R^4=Me$	161—162	4.5	[34]
11	R—CD=$\overset{+}{N}$Me$_2$ $PO_2Cl_2^-$, NaSH	 (XXXII)			
		a: $R^1=R^2=H$	102—104	78	[34]
		b: $R^1=R^2=Me$	168—170	83	[34]
12	R—CH=$\overset{+}{N}$Me$_2$ $PO_2Cl_2^-$, NaSH (XXVII)	 (XXIXa)	160 (decomp.)	86	[33]
13	R—CH=$\overset{+}{N}$Me$_2$ ClO_4^-, NaSH (XXXIVa, b)	 (XXXIIIa)	>215 (decomp.)	44	[35]
		 (XXXIIIb)	>215 (decomp.)	43	[35]
14	 (XXXV)	 (XIIb)	88—89	33	[28,33]
15	R—CH=$\overset{+}{N}$Me$_2$$PO_2Cl_2^-$, NaSH (XXXVII)	 (XXXVI)			
		a: $R_2^1=(CH_2)_2O(CH_2)_2$, $R^2=R^3=Ph$	170—171	61	[36]
		b: $R_2^1=(CH_2)_4$, $R^2=R^3=Ph$	163.5—164	33	[36]
		c: $R_2^1=(CH_2)_2O(CH_2)_2$, $R^2=Ph$, $R^3=H$	139—140	27	[36]
		d: $R_2^1=(CH_2)_2O(CH_2)_2$; R^2, $R^3=(CH_2)_3$	116—117	50	[36]
		e: $R_2^1=$cyclo-C_6H_{11}, $R^2=R^3=Ph$	136.5	23	[36]

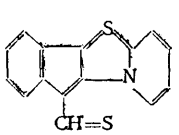
Table 1 (contd)

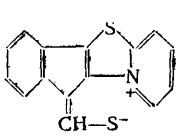
No.	Reagents	R–CH=S	M.p., °C	Yield, %	Refs.
16	 (XLV)	 (XLVI)			
		a: R=H, $R^1=R^2$=COOMe	88	70; 75	[40, 42]
		b: R=Me, $R^1=R^2$=COOMe	123–126	75	[42]
		c: R=Ph, $R^1=R^2$=COOMe	152–154	85; 70	[40, 42]
		d: R=Ph, $R^1=R^2$=COOEt	130–134	75	[42]
		e: R=Ph, R^1=H, R^2=COOMe	124	50	[42]
		f: R=Me, R^1=H, R^2=COPh	156 decomp.–274	40	[42]
		g: R=R^1=H, R^2=COPh	152 decomp.–198	70	[42]
		h: R=H, $R^1=R^2$=COPh	143	74; 70	[40, 42]
		i: R=Ph, $R^1=R^2$=COPh	—	63; 71	[39, 40]
17	 (XLIX)	 (La, b) $n = 2, 3$	—	60–80	[43]
18	PhCO–C(Ph)=CHCl, Na_2S	PhCO–CH(Ph)–CH=S ⇅ PhCO–C(Ph)=CH–SH (LI)	84–86	30	[44]
19	$PhCOCH_2SCH_2$–C$(CH_3)_3$ (LXXIV)	$(CH_3)_3C$–CH=S (LXXIII)	—	~50	[65]
20	R–Li, EtO–CH=S (LXXVI)	$(Me_3Si)_3C$–CH=S (LXXV)	129–131	16	[17]
21	R–Li, EtO–CH=S (LXXVIII)	2,4,6-(t-Bu)$_3C_6H_2$–CH=S (LXXVII)	146–147	56	[16]
	R–CH=NNH_2, S_2Cl_2 (LXXIX)	»	—	40	[16]

The deuteriated TA (XXXIIa, b) were synthesised from the corresponding pyrrolo[2,1-*b*]thiazoles using [$^2H_7$]dimethylformamide and phosphoryl chloride in 1,2-dichloroethane for studies by NMR and IR spectroscopy.[34]

The synthesis of stable thioformyl derivatives of 10*H*-indeno-[2,1-*d*]-pyrido-[2,1-*b*]thiazole (XXXIIIa, b) has also been reported.[35] Instead of DMF, dimethylthioformamide was used, which made it possible to increase the yield of the salts (XXXIVa) and (XXXIVb) from 63 and 40% to 93 and 87% respectively. This can be explained by the different formylating capacities of the ion-pair reaction intermediate $Me_2\overset{+}{N}CH-XPOCl_2Cl^-$, where X = S or O.[35]

The neutral structure (A) of the thioaldehyde (XXXIIIa), formally containing a tetracovalent endocyclic sulphur atom, is undoubtedly stabilised by the formation of the resonance zwitter-ion (B).[35]


(A), (XXXIIIa)

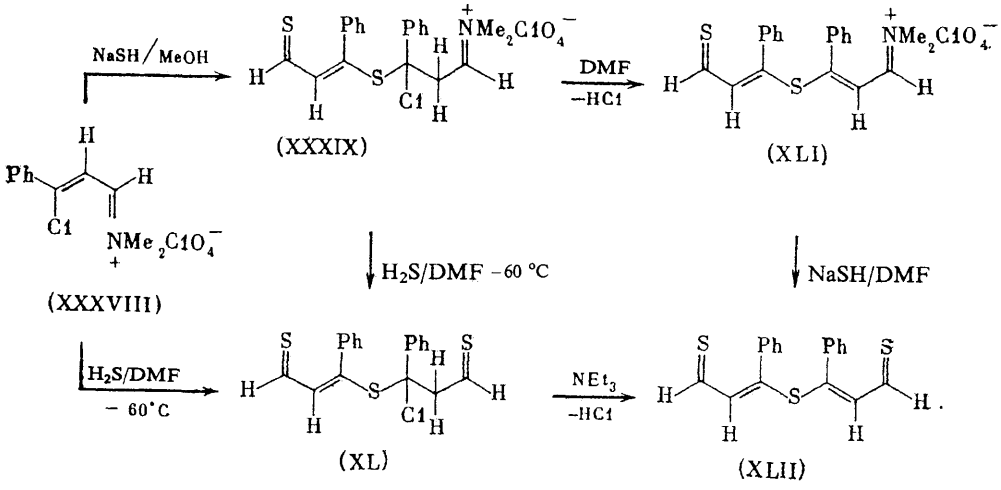

(B), (XXXIIIa)

A method of synthesis of thioformylindolizines (XII) from ethoxymethyleneindolizinium salts (XXXV) has been proposed.[28,33] It is based on the condensation of 3*H*-indolizinium perchlorates with triethyl orthoformate and subsequent treatment of the resulting salts (XXXV) with sodium hydrogen sulphide.

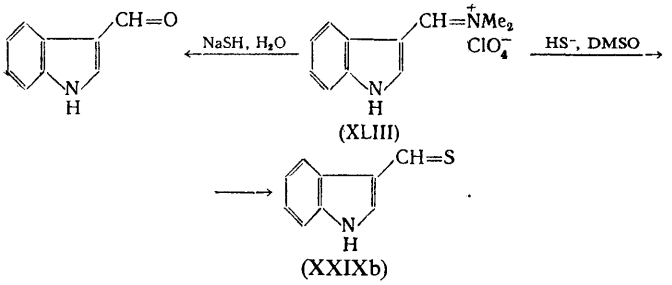
A single-stage method of synthesis of aliphatic and alicyclic enaminothioaldehydes (XXXVI), involving the successive treatment of the enamines (XXXVII) with DMF, $POCl_3$, and NaSH, has been described recently.[36] The thials (XXXVI) are orange or red crystalline substances which are stable for several months even at room temperature.

New synthetic possibilities for the hydrothiolysis of salts of the type (XXXVIII) have been demonstrated.[37] Depending on the character of the ion-pair states of the reactant and temperature, the hydrothiolysis of 3-chloro-*NN*-dimethyl-3-phenylprop-2-en-1-yliminium perchlorates (XXXVIII) leads to the asymmetric sulphides (XXXIX) or (XL). Their dehydrohalogenation products

are 1,7-bishetero-substituted dipropenyl sulphides (XLI) and (XLII) respectively:

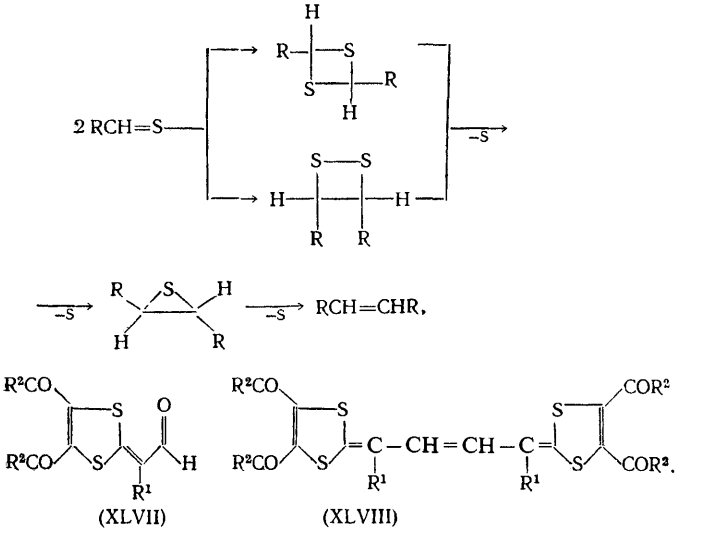


Under the conditions of the synthesis of 3-thioformyl derivatives of indole and indolizine by treating the corresponding methyleneiminium salts with an aqueous solution of sodium hydrogen sulphide,[33] *N*-[(3-indolyl)methyl]-*NN*-dimethyliminium perchlorate (XLIII) hydrolyses to 3-formylindole.[38] The hydrothiolysis of the salt (XLIII) can be readily achieved by treatment with anhydrous NaSH or hydrogen sulphide in dimethyl sulphoxide at 20 °C and leads to the formation of 3-thioformylindole (XXIXb) in solution:



4. Alkynylation of 1,2-dithiole-3-thiones

[2 + 3]Cycloaddition of acetylenedicarboxylic acid esters (XLIV, $R^1 = R^2$ = COOMe or COOEt) or dibenzoylacetylene (XLIV, $R^1 = R^2$ = COPh) as well as other activated acetylenes to 5-unsubstituted 1,2-dithiole-3-thiones (XLV) leads to 2-thioformylmethylene-1,3-dithioles (XLVI)[39–42] (Table 1, No. 16). These substances almost always contain an admixture of the isostructural aldehyde (XLVII). A long reaction time (24 h) as well as refluxing of the TA (XLVI) in benzene lead mainly to the alkenes (XLVIII)—the products of the bimolecular elimination of thial sulphur in accordance with the scheme[40]



5. Aminolysis of 1,2-dithiolium salts

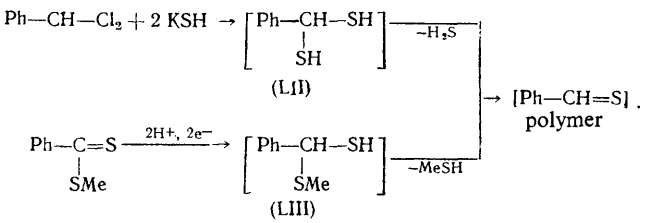
Treatment of 1,2-dithiolium salts (XLIX) at 25 °C with an equivalent amount of ethylenediamine in ethanol or of trimethylenediamine in benzene leads to the stable TA (La, b)[43] (Table 1, No. 17). This reaction opened a convenient synthetic route to 14-, 15-, and 16-membered tetraazamacrocycles.[43]

6. Hydrothiolysis of 1-chloro-2-benzoylstyrene

The hydrothiolysis of alkenyl chlorides is a widely used approach to the synthesis of thiocarbonyl compounds.[11] 2-Oxo-1,2-diphenyl-1-thioformylethane (LI), which exists in the stable alkenethiol tautomeric form[44] (Table 1, No. 18), has been obtained in this way.

7. The cleavage of *gem*-dithiols and their derivatives

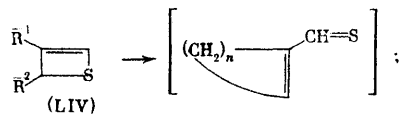
gem-Dithiols and their S-derivatives can be cleaved at one of the C–S bonds with formation of the thiocarbonyl group.[45] Thus the *gem*-dithiol (LII), obtained from benzylidene dichloride and potassium hydrogen sulphide, is readily converted into thiobenzaldehyde.[45] The primary product (LIII) of the reduction of methyl dithiobenzoate splits off methanethiol and is also converted into thiobenzaldehyde, which immediately polymerises.[45]



Certain 1,3,5-trithianes are readily cleaved on heating to the initial TA.[6,9,11,46] This can be used for the "storage" of the corresponding TA as trimers in order to investigate them subsequently.

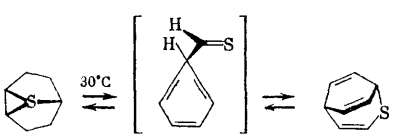
8. Rearrangement of cyclic sulphides

The spontaneous decomposition of certain 3,4-disubstituted thiets (LIV) begins with ring opening and the formation of αβ-unsaturated TA (LV), which rapidly polymerise.[47,48] When compounds (LV, n = 4, 5) were allowed to interact with 2,4-dinitrophenylhydrazine, the hydrazones of 2-thioformylcyclohexene and 2-thioformylcycloheptene were isolated.[47]



$R^1 = R^2 = (CH_2)_4$.
$R^1 = R^2 = (CH_2)_5$

1-Thioformylcycloheptatriene (LVI) is an active intermediate in thermal isomerisation via the mechanism[49]



9. Thermolysis of Unsaturated Sulphides

The synthesis of two extremely reactive compounds—thioacrolein and thiobenzaldehyde—has been achieved by the flash thermolysis of diallyl sulphide and allyl benzyl sulphide respectively.[50–53] According to IR spectroscopic data, thioacrolein begins to change slowly already at 77 K, while thiobenzaldehyde persists up to 110 K.[50]

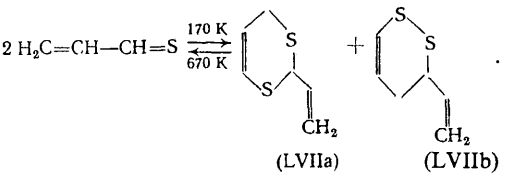
$$H_2C{=}CHCH_2{-}S{-}CH_2CH{=}CH_2 \xrightarrow{\Delta} [CH_2{=}CH{-}CH{=}S],$$

$$PhCH_2{-}S{-}CH_2CH{=}CH_2 \xrightarrow{\Delta} [Ph{-}CH{=}S].$$

Thioacrolein was identified in the thermolysis products of diallyl sulphide (550 °C, 10–50 mmHg) by microwave spectroscopy.[51] Under normal conditions, this thial persists for 1–2 min.

The use of photoelectron spectroscopy (interpretation of "molecular fingerprints") during thermolysis made it possible to determine the optimum temperature at which thioacrolein is formed from diallyl sulphide (660 K).[52,53]

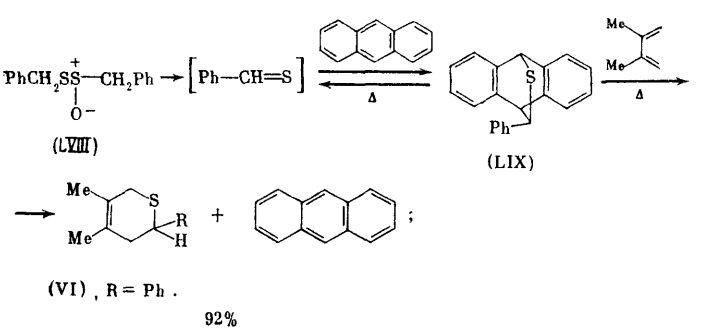
The photoelectron spectrum of monomeric thioacrolein was obtained in a study of the thermolysis products of the Diels–Alder dimers (LVIIa, b). This thermal reaction made thioacrolein available for preparative purposes and further spectroscopic studies.[52,53]



10. The cleavage of disulphides and their derivatives

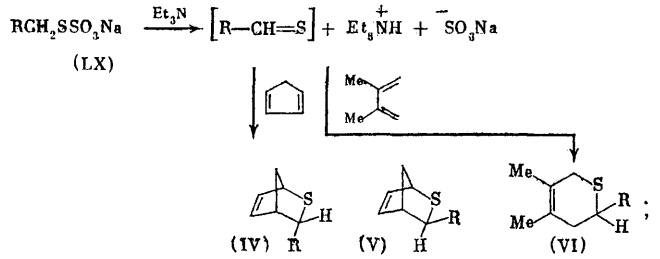
New precursors of TA have been discovered in recent years.[20,21,54] In particular, these proved to be alkyl thiosulphinates, whose thermolysis has become a general and convenient method of synthesis of TA.[54,55] Thus, when *S*-benzyl phenylmethanethiosulphinate (LVIII) is heated in toluene at 100 °C, thiobenzaldehyde is formed. The blue colour which its presence imparts to the reaction mixture [UV spectrum: λ_{max} = 580–590 and 610 nm (shoulder), which corresponds to the spectrum at 77 K of thiobenzaldehyde obtained by the vacuum flash pyrolysis of allyl benzyl sulphide[50]] vanishes after 15 min at 20 °C.[54]

The thermolysis of the thiosulphinates (LVIII) is usually carried out in the presence of dienes of anthracene, which are TA "trapping agents".[54,55] The adduct with anthracene (LIX) (97% yield) can itself serve as a source of thiobenzaldehyde. When it is heated in the presence of 2,3-dimethylbutadiene in a sealed tube, the 2*H*-dihydrothiane (VI) and anthracene are formed.



The readily available Bunte salts (LX) are very convenient for the synthesis of TA with electron-accepting substituents.[20] They readily undergo 1,2-elimination on treatment with triethylamine and calcium chloride. The corresponding cyclic adducts (IV)–(VI) were obtained from them in the presence of conjugated dienes. Under these conditions, sodium *S*-4-nitrobenzyl thiosulphate (LXe) gives rise to the adduct (IV)–(VI) in high yields. On the other hand, the unsubstituted benzyl derivative (LXd) does not afford such adducts at all. This example demonstrates the significant role of the CH acidity of the methylene group in compound (LX) and shows that the conjugation of the thioformyl functional group with the benzene

ring cannot by itself ensure the 1,2-elimination process.[20]

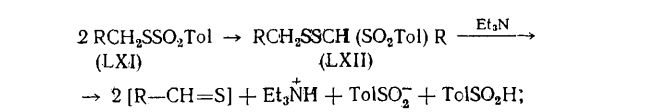


R = Et–CO (a), (Sect.III), Ph–CO (b), (Sect.III), PhNH–CO (c) (Sect.III), Ph (d), 4-$NO_2C_6H_4$ (e).

In methanol at 20 °C, thials react with cyclopentadiene to form the adducts (IV) and (V) in high yields (66–86%), while the reaction with 2,3-dimethylbuta-1,3-diene produces adducts in a lower yield. In a less polar system (benzene–ethanol), the yield of the adducts (VI) rises to 55–65%. The competitive attack by nucleophiles (for example, SO_3^{2-}) on the TA is probably lessened under these conditions.

The ability of the adducts (IV)–(VI) to dissociate on heating makes them valuable sources of reactive TA.[20]

Toluene-*p*-thiosulphonates (LXI) are readily converted into α-sulphonyl disulphides (LXII) which are cleaved with formation of TA on treatment with triethylamine similarly to the Bunte salts:[21]

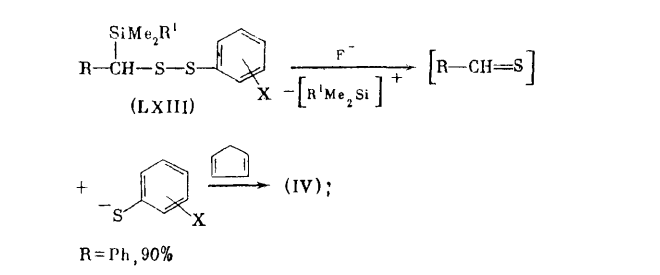


R = EtO–CO (a) (Sect.III), 4-BrC_6H_4–CO (b) (Sect.III), Ph (c), 4-$NO_2C_6H_4$ (d); Tol = 4-MeC_6H_4.

The disulphides (LXIIa, b, d) react with triethylamine at 20 °C and with a solution of cyclopentadiene in benzene to form the corresponding adducts (IV) and (V), the *endo*-isomer (IV) predominating. Among the starting compounds, the benzyl derivative (LXIIc) is least reactive. Nevertheless, it forms the adducts (IVc) and (Vc) in acetonitrile.

This new TA generating reaction has been called a fragmentation–elimination process via a concerted mechanism.[21]

An elegant and general method of synthesis of thioformyl compounds from aryl[α-(dimethylorganylsilyl)organylmethyl] disulphides (LXIII) has been proposed recently.[56] On treatment with the F^- anion, the disulphides are readily cleaved to the corresponding TA and the arenethiolate anion.



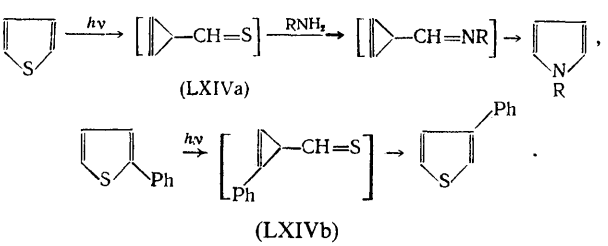
The effectiveness of the cleavage is determined by the stability of the arenethiolate leaving group. 2,4,6-Trichlorophenyl disulphides (LXIII, X = 2,4,6-trichloro-group) are extremely unstable. The 2-nitro-4-chloro-derivatives (LXIII, X = 2-NO_2 or 4-Cl) are extremely reactive, while the unsubstituted disulphides (LXIII, X absent) are cleaved only on heating.

The rate of fragmentation-elimination is also influenced by the reactivity of the source of the fluoride ion. In the presence of 18-crown-6, CsF or KF generate TA slowly at 20 °C, while tetrabutylammonium fluoride ($NBu_4^+F^-$) in tetrahydrofuran acts rapidly in the temperature range from 0 °C to –78 °C.

Thiobenzaldehyde adds to cyclopentadiene, forming a mixture of the cyclic *exo*- and *endo*-adducts (V) and (IV) in proportions of 1 : 7. The predominance of the *endo*-isomer can be due to the kinetic factor, but Dreiding models show that the *endo*-isomers are sterically less hindered and should therefore be more stable.[56]

11. Photochemical methods

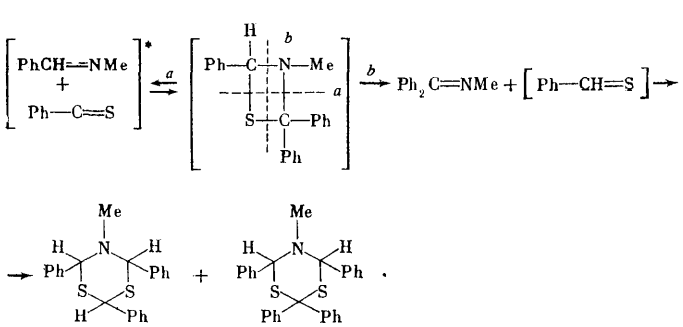
Certain types of conjugated TA are generated in photochemical reactions and play an important role in them.[8,57,58] Thus 3-thioformylcyclopropene (LXIVa) is an intermediate in the photolytic conversion of thiophen into *N*-alkylpyrroles in the presence of amines.[57] The formation of 1-thioformyl-2-phenylcyclopropene (LXIVb) has been explained by the rearrangement of 2-phenylthiophen to 3-phenylthiophen under the influence of UV irradiation.[58]



(LXIVa)

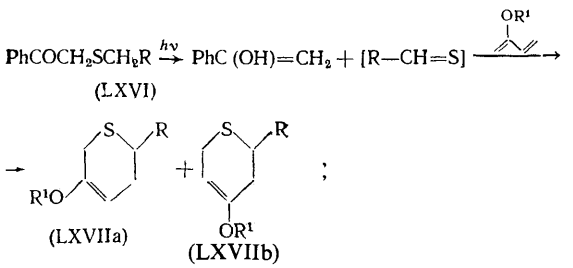
(LXIVb)

The formation of a polymer in the photolysis of ω-benzylthioacetophenones is apparently due to the intermediate generation of the monomeric thiobenzaldehyde.[8] The same TA is probably an intermediate in the formation of substituted 1,3,5-dithiazines (LXVa, b) and benzophenone methylimine from photoexcited thiobenzophenone and benzaldehyde *N*-methylimine.[8]



(LXVa) (LXVb)

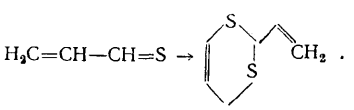
A simple method of synthesis of dienophilic TA by irradiating a mixture of organyl phenacyl sulphide (LXVI) with a diene at 0 °C has been developed recently.[59,60]



(LXVI) (LXVIIa) (LXVIIb)

R=H, Ph, Me—CO, Ph—CO, CN, AlkO—CO, Ph_2PO, $PhSO_2$, EtO—CO—CH=CH; $R^1 = SiMe_2$—t-Bu.

The use of the most reactive dienes (for example, Danishevskii's diene)‡ makes it possible to "trap" the "exotic" thioformylsulphone ($PhSO_2$—CH=S) and thioformylphosphine oxide (Ph_2PO—CH=S), whose oxygen analogues are unknown.[60] In the case of the αβ-unsaturated TA (EtO—CO—CH=CH—CH=S), the yield of the adduct (LXVIIa) is low (10%), although the products of the self-condensation of this thial have not been detected. Under analogous conditions, thioacrolein cannot be trapped by the usual dienes, since it is stabilised as the dimer—2-vinyl-1,3-dithiene:[59]

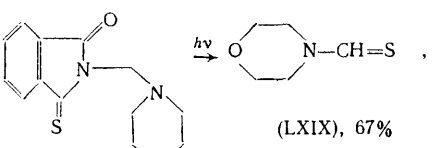


An excess of the diene and carefully purified reagents are necessary for the synthesis of the adducts (LXVII) in order to reduce to a minimum the catalytic thial self-condensation.[60] The yields of the adducts of TA with electron-donating substituents depend significantly on the structure of the diene, the nature of the substituent R in the TA, and the reaction conditions.

The regiospecificities of the cyloaddition of the compounds R—CH=S containing electron-accepting or electron-donating substituents R are not the same. In the presence of electron-accepting substituents, TA react like carbon dienophiles. Otherwise they behave similarly to carbonyl dienophiles. This difference agrees with quantum-chemical calculations.[60]

By virtue of the different regioselectivities of the reactions of dienes with TA having electron-donating or electron-accepting substituents, a large series of dihydrothiopyrans have become available.[61]

The photolytic cleavage of *N*-(*N*-morpholinomethyl)thiophthalimide (LXVIII) to the *N*-thioformylamine (LXIX),[62] which belongs to the class of the simplest thioformamides, proceeds in an unusual manner. The initial stage of this process is apparently the elimination of a proton from the methylene bridge.

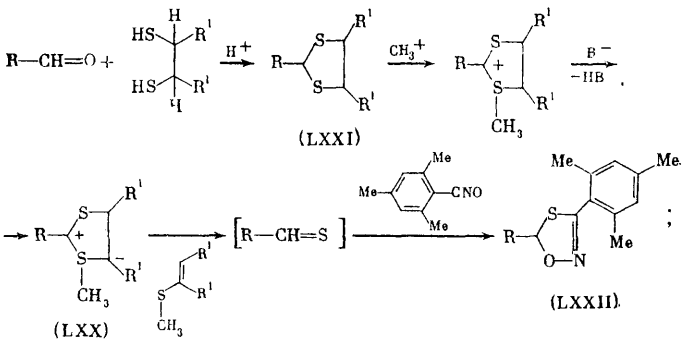


(LXVIII) (LXIX), 67%

‡CH_2=CH(OSiMe$_3$)—CH=CH—OMe.

12. Fragmentation of S-ylides

A novel method of synthesis of TA, based on the fragmentation of S-ylides of type (LXX), generated from an aldehyde (the oxygen analogue of the target TA) via the 1,3-dithiolan (LXXI), was proposed in 1985.[63] It proceeds in accordance with the scheme



(LXXI) (LXX) (LXXII)

R = Ph, H_2C=CH.....

The TA obtained react with mesitonitrile *N*-oxide to form stable 1,4,2-oxathiazoles (LXXII). In the absence of a "trapping agent", polymers or trimers are formed. In order to obtain thioacrolein, it is sufficient to treat its precursor—1,3-dithiolan (LXXI, R=CH=CH_2, R^1 = COOMe)—with lithium diisopropylamide. Thus 1,3-dithiolans are convenient reagents for the single-stage synthesis of highly reactive TA.[63,64]

This method harmoniously supplements the photochemical[59,60] or thermochemical[50–53] approaches to the synthesis of TA. It provides greater synthetic possibilities than does the 1,2-elimination induced by a base[20,21] or the cleavage of aryl [α-(dimethylorganylsilyl)-organylmethyl] disulphides.[56]

V. Sterically stabilised thioaldehydes

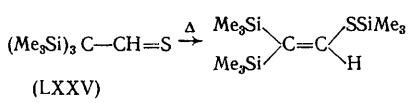
For more than 100 years, the attempts to obtain monomeric aliphatic TA were unsuccessful.[6,11] It was not until 1983 that it was possible to synthesise the first long-lived aliphatic TA—2,2-dimethylpropanethial (LXXIII).[65] The starting material for its synthesis was neopentyl phenacyl sulphide (LXXIV), whose photolysis in benzene in the presence of 5% of 2,3-dimethylbutadiene leads to the polymer [t-BuCH—S—]$_n$ in 60% yield. When this polymer is heated *in vacuo* (≥ 250 °C), 2,2-dimethylpropanethial (LXXIII) is formed (Table 1, No. 19).

The lifetime of this TA in chloroform, benzene, methylene chloride, or ether at 20 °C reaches 16 h. The relative stability of the TA (LXXIII) is probably determined not only by the bulky t-butyl group but also by the purity of the starting materials, which rules out the catalytic self-reactions of the thial. Indeed, its lifetime in a chloroform—ethanol mixture (15 min) falls to 5 min after the addition of trieythylamine and to several seconds in the presence of traces of HCl. The monomeric trimethylpropanethial (LXXIII) and its solution are extremely stable in air.

The first stable aliphatic Si-functional TA—tris(trimethylsilyl)-ethanethial (LXXV)—has been described recently.[17] Its synthesis is based on the reaction of tris(trimethylsilyl)methyllithium (LXXVI) with *O*-ethyl thioformate in tetrahydrofuran at –78 °C (10 min) and further at 20 °C (1.5 h) (Table 1, No. 20).

The thial (LXXV) is a pink-red crystalline compound which can be stored for a long time in the refrigator without changes and is

stable in air at 20 °C for about a week. This compound can be purified by column chromatography on silica gel or by freezing out from pentane at −78 °C. At ~80 °C, the TA (LXXV) rearranges quantitatively to 1,1-bis(trimethylsilyl)-2-trimethylsilylthioethene:



(LXXV)

The first stable *exo*-substituted thiobenzaldehyde—2,4,6-tris-t-butylthiobenzaldehyde (LXXVII)—was obtained by the reaction of 2,4,6-tri(t-butyl)phenyllithium (LXXVIII) with *O*-ethyl thioformate in tetrahydrofuran followed by chromatographic purification.[16] Another route to the synthesis of the TA (LXXVII) is based on the reaction of the hydrazone (LXXIX) with sulphur dichloride in the presence of triethylamine[16] (Table 1, No. 21).

The thial (LXXVII) is a strikingly stable purple crystalline compound which can be preserved for about a year at 20 °C or for two weeks on refluxing in benzene without access by air. The unsubstituted thiobenzaldehyde polymerises already at −160 °C.[50]

VI. Physical properties of compounds with the thioaldehyde group

According to microwave specroscopic data, the C=S bond length in the monomeric thioformaldehyde is 1.6108 Å.[66] This is longer than the C=O bond length in formaldehyde (1.2083 Å)[66] and is consistent with the predicted interatomic distance in the unperturbed thiocarbonyl group (1.607 Å).[11] The calculated dipole moment of thioformaldehyde is 1.6474(14) D.[67] Since μ for gaseous $CH_2=O$ is 2.27 D,[68] this shows that the polarity of the C=S bond is smaller than that of the C=O bond.

It has been established by microwave spectroscopy that the thioacrolein molecule is planar and has a dipole moment of 2.61 D.[51]

The photoelectron spectra of thioacrolein and acrolein are almost the same with ionisation peaks at 8.87 and 10.2 eV respectively.[52]

It is remarkable that the mass spectra of heterocyclic TA, namely 1,2-dimethyl-3-thioformylindole (XXIXa), 2-methyl-3-thioformylindolizine (XIIb), and 6-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole (XXVIIIa), are characterised by an intense $(M-45)^+$ peak corresponding to the loss of the thioformyl group.[33]

The position of the absorption band of the thiocarbonyl group in the IR spectra (1100−1270 cm^{-1}) has now been reliably established as a result of the successful development of the chemistry of thioketones.[11]. The C=S bond stretching vibrations in the spectra of TA are in the same region. Thus the band at 1063 cm^{-1} corresponds to the absorption of the thiocarbonyl group in the IR spectrum of thioformaldehyde in an inert gas matrix at 14 K.[69] The absorption bands of the C=S group in the spectra of sterically stabilised TA, i.e. $Me_3C-CH=S$ (LXXIII) and $(Me_3Si)_3C-CH=S$ (LXXV), are at 1085 and 1120 cm^{-1} respectively.[17,65] The IR spectra of the stable heterocyclic TA (XXIXa), (XII), and (XXVIII) contain an intense band in the range 950−985 cm^{-1}.[33] The study of the solvent effect led to its assignment to the C=S bond vibration. In the spectrum of the TA (XXIXa), this band shifts from 978 cm^{-1} in cyclohexane to 956 cm^{-1} in 1,1,2,2-tetrabromoethane.[33] In the spectrum of the enaminothioaldehyde (XIII), the band at 1260 cm^{-1} corresponds to the ν(C=S) vibration.[29]

The electronic spectra of TA are characterised as a rule by three absorption regions due to the $n \rightarrow \pi^*$ transition in the visible part of the spectrum and the $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions in the UV region. The electronic spectra of stable heterocyclic TA—thioformylindolizines (XII)[28] and thioformylpyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI)[34]—have been studied in detail. Thus the spectra of 3-thioformylindolizines (XII) contain four groups of intense maxima in the ranges 420−460, 300−325, 250−275, and 205−230 nm ($lg\varepsilon > 3.7$). Three intense absorption regions can be observed in the spectra of 1-thioformylindolizines (XXX): 420−460, 260−280, and 210−240 nm. The difference between the overall forms of the spectra makes it possible to recognise readily 1- and 3-thioformylindolizines.[28] The spectra of 3-thioformylindolizines (XII) are characterised by two broad low-intensity bands (~520 and ~550 nm) ($lg\varepsilon$ = 1.9−2.2), which do not have a distinct minimum. These bands undergo a hypsochromic shift with increase in solvent polarity and belong to the $n \rightarrow \pi^*$ transition in the thiocarbonyl group. The cause of the multiplicity of the spectrum still remains obscure. The spectrum of 2-t-butyl-1-thioformylindolizine (XXXa) in cyclohexane has a very broad $n \rightarrow \pi^*$ band with λ_{max} = 534 nm ($lg\varepsilon$ = 1.84) and a shoulder at ~570 nm, while in the spectrum of 2,3-dimethyl- 1-thioformylindolizine (XXXb) there is a similar band in the range from ~510 to 560 nm ($lg\varepsilon \simeq 1.9$).[28]

The electronic spectra of thioformylpyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI)[34] and of 3-thioformylindole (XXIXb)[38] have a similar line form and the nature of the bands is likewise similar.

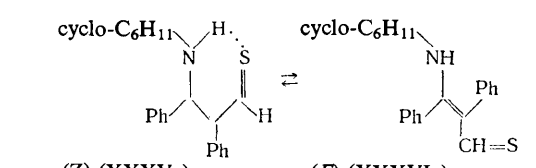
The electronic spectra of the sterically stabilised TA are characterised by the following parameters [the compound, λ_{max} (nm) (ε) the solvent, and the literature reference are quoted in succession]: $(CH_3)_3C-CH=S$, 508(16) (MeCN);[65] $(Me_3Si)_3C-CH=S$, 518(15), 272(9940), 212(4320) (C_6H_{12}); 503(14), 277(8720), 211(5330) (MeCN);[17] 2,4,6-t-$Bu_3C_6H_{12}-CH=S$, 564(19), 338(1850) (C_6H_{12}); 552(19), 340(1690) (EtOH).[16]

The spectra of the labile thioacrolein and thiobenzaldehyde have been recorded at 77 K under specially selected conditions.[50] The calculated values of λ_{max} agree very well with the experimental data.

	λ_{max} (found)			λ_{max} (calc.)		
	$n\rightarrow\pi^*$	$\pi\rightarrow\pi^*$	$n\rightarrow\sigma^*$	$n\rightarrow\pi^*$	$\pi\rightarrow\pi^*$	$n\rightarrow\sigma^*$
$CH_2=CH-CH=S$	580	276	—	570	265	—
$C_6H_5-CH=S$	575	320	228	567	302, 296	231, 226

In the ^1H NMR spectra of thioaldehydes, the signal of the thioformyl proton is in a low field within a fairly wide range [δ(p.p.m.) ranges from 9 to 13].[17,28,29,33,34,36,38–40,42,65] It is believed that 2,4,6-tri(t-butyl)thiobenzaldehyde (LXXVII) contains the "purest" thioformyl group whose proton signal is at δ = 13.02 p.p.m.[16]

According to ^1H NMR spectroscopic data, the enaminothial (XIII) exists to the extent of 95% as the rotational *S-trans*-isomer with a barrier to the unhindered rotation about the C−N bond of 17.1 kcal mol^{-1} at the coalescence temperature of 330 K.[29]



(Z)-(XXXVe) (*E*)-(XXXVIe)

δ, p.p.m. 15.24 (NH) 5.41 (NH)

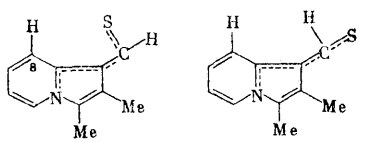
9.82 (CH=S) 9.95 (CH=S)

The thioaldehydes (XXXVIa–d) and (*Z*)-isomers and their structure corresponds to that of the initial enamines. The cyclohexylamino-substituted TA (XXXVIe) contains ~10% of the (*E*)-isomer.[36]

The ^{1}H NMR spectra of the thioformylindolizines (XII) and (XXX) have been investigated in detail.[28] The 1- and 3-thioformyl groups exert a strong diamagnetic anisotropic deshielding effect on the H(8) and H(5) atoms respectively located on the opposite side. The H(5) chemical shifts in the spectra of 3-thioformylindolizines (XII) are in the range δ = 11.1–11.6 p.p.m. In 2,3-dimethyl-1-thioformylindolizine (XXXb), the rotation about the ring–CH=S bond is hindered. This can be explained by the appreciable contribution of the dipolar mesomeric form (B):[28]

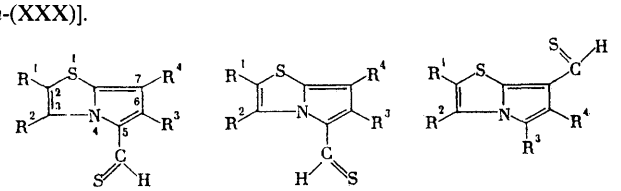
$$\underset{(A)}{R{-}CH{=}S} \leftrightarrow \underset{(B)}{\overset{+}{R}{=}CH{-}S^-}$$

Pronounced deshielding of H(8) and the singlet signal of the thioformyl proton show that below the coalescence temperature, the TA (XXXb) exists exclusively in the *syn*-configuration, which is more stable than the *anti*-form. This is determined by the intramolecular electrostatic attraction between the charges on the sulphur atom and the pyridine ring, which corresponds to a minimum in the potential energy of the molecule.[28]



syn-(XXXb) *anti*-(XXXb)

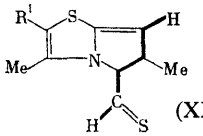
The temperature dependence of the ^{1}H NMR spectra shows that the rotation about the heterocyclic-CH=S bond is hindered in thioformylpyrrolo[2,1-*b*]thiazoles (XXVIII) and (XXXI).[34] These data agree with the existence of the 5-thioformyl derivatives (XXVIII) ether in the *syn*-configuration [compounds (XXVIIIa–d)] or in the *anti*-configuration [compounds (XXVIIIe, f)], while the 7-thioformyl derivatives exist only in the *syn*-configuration [*syn*-(XXX)].



syn-(XXVIII) *anti*-(XXVIII) *syn*-(XXX)

	syn-(XXVIII)				*anti*-(XXVIII)				
	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
a	H	H	Me	H	e	H	Me	Me	H
b	Me	H	Me	H	f	Me	Me	Me	H
c	H	H	Me	Me					
d	H	Me	t-Bu	H					

The higher stability of the 5- and 7-*syn*-thioformyl derivatives relative to their *anti*-isomers is a consequence of the intramolecular electrostatic attraction of the partial charges on the sulphur atom of the thioformyl group and on the thiazole ring. Compounds (XXVIIIe, f) exist preferentially in the *anti*-form owing to the steric effect of the 3-methyl substituent, which repels the thioformyl sulphur atom from the plane of the ring. In compounds (XXVIIId), the effect of the t-butyl group is superimposed on that of the 3-methyl group, which forces the thioformyl group into the *syn*-configuration. The presence of the long-range spin–spin H(7)–CH=S interaction [the spin–spin coupling constant (SSCC) is 0.8 Hz] in the thioaldehydes (XXVIIIe, f) constitutes additional demonstration of their existence in the *anti*-form. In these TA, the H(7)–CH=S protons are disposed in the *W*-configuration (*W*), which is most favourable for the effective interaction through the conjugated system.[34]



(XXVIII), R^1 = H (e) or Me (f)

(*W*)

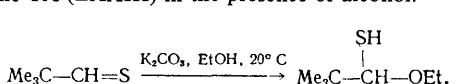
The ^{13}C NMR spectroscopic data for thioaldehydes are extremely limited. However, the existing information shows that the carbon nucleus of the ^{13}C=S moiety of the thioformyl group resonates in the region characteristic of thioketones.[11,16,17,70]

VII. Chemical properties of thioformyl compounds

The high reactivity of thioaldehydes can be inferred even from their extremely high tendency to undergo trimerisation, oligomerisation, and polymerisation. Not only the structure but also the conditions of the synthesis of TA determine the yield of particular products. Thus the synthesis of thioformaldehyde from formaldehyde and hydrogen sulphide in the presence of HCl leads mainly to the formation of the cyclic trimer (1,3,5-trithiane), while in an alkaline medium readily fusible polymers have been obtained.[71] The synthesis of thiobenzaldehyde from benzaldehyde and H_2S in a highly acid medium leads mainly to the more stable β-isomer; a weakly acid medium and a low reaction temperature afford not only greater amounts of the α-isomer but also a greater amount of the polymer with a molecular weight of ~1000.[71]

It has been convincingly demonstrated[72] that the self-transformations of the monomeric TA are catalytic processes. The addition of protic or Lewis acids induces the instantaneous trimerisation and polymerisation of 2,2-dimethylpropanethial (LXXIII) in all solvents. The authors explain by this observation the failure of many investigators to detect monomeric TA in the acid-catalysed thionation of aldehydes.

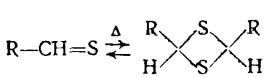
The decomposition of TA is also promoted by basic catalysts (triethylamine, K_2CO_3). Small amounts of the thioacetal (LXXX) and the isomeric 1,3,5-trithianes are formed under these conditions from the TA (LXXIII) in the presence of alcohol.[72]



(LXXIII) (LXXX)

In pure ether and chloroform, the TA (LXXIII) exists for a long time in the monomeric state but hydroxylated solvents induce its rapid trimerisation.[72]

Like non-enolisable thioketones, TA undergo reversible "head to tail" thermal dimerisation.[73]



R=Alk, Ar.

Thioacrolein is stabilised as the dimer (1,3-dithietan)[59] (see Section IV); dithianes can lose their thial sulphur and can be converted into symmetrically substituted ethylenes.[40] However, evidence for the formation of a dimeric product from 2,2-dimethylpropanethial (LXXIII) has not been obtained.[72]

TA are reactive in various reactions with nucleophiles. The aminolysis of the intermediate thioformaldehyde is an important step in the reactions of methanesulphenyl halides with secondary amines.[7]

$$[H{-}CH{=}S] \xrightarrow{R_2NH} (R_2N)_2CH_2 + H_2S.$$

Benzoylthioformaldehyde and morpholine, formed on decomposition of the sulphenamide (LXXXI), immediately react to form the *gem*-aminothiol (LXXXII).[74]

$$Ph{-}CO{-}CH_2{-}S{-}N(CH_2)_4 \rightarrow Ph{-}CO{-}CH{=}S + HN(CH_2)_4 \rightarrow Ph{-}CO{-}CH(SH){-}N(CH_2)_4$$

(LXXXI) (LXXXII)

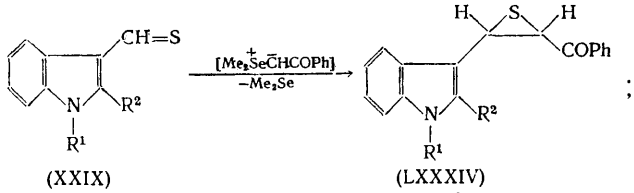
The *gem*-aminothiols (LXXXIII) are readily formed from thioformylimines and ammonia.[74]

$$R{-}C(=NH){-}CH{=}S \xrightarrow{NH_3} R{-}C(=NH){-}CH(SH){-}NH_2$$

(LXXXIII)

Like thioketones, thioaldehydes give rise to hydrazones and semicarbazones.[32,38]

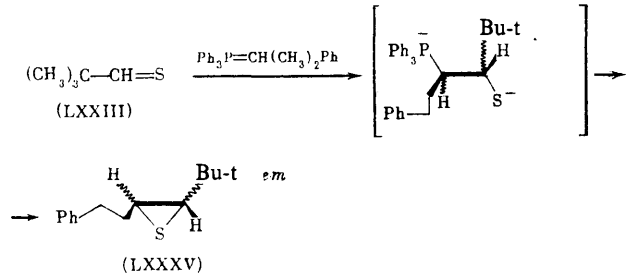
Ylides behave as nucleophiles in reactions with thiocarbonyl compounds.[11] The interaction of 3-thioformylindoles (XXIX) with dimethylselenonium benzoylmethylide takes place readily in solution in DMF at 0 °C and leads to 3-benzoyl-2-indolythiirans (LXXXIV).[75]



(XXIX) (LXXXIV)

$R^1 = R^2 = Me$ (a); $R^1 = R^2 = H$ (b); $R^1 = H$, $R^2 = Me$ (c).

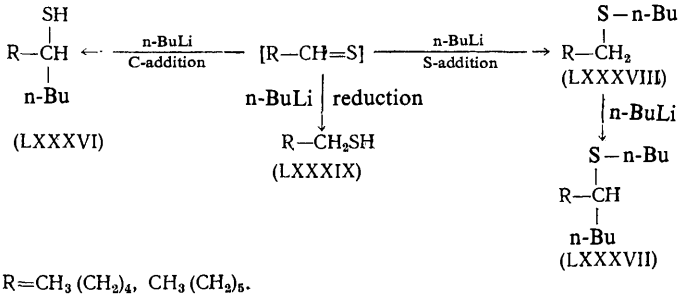
2,2-Dimethylpropanethial (LXXIII) reacts with (3-phenylpropylidene)triphenylphosphorane to form the thiiran (LXXXV).[72]



(LXXIII) (LXXXV)

The reactions of thioketones with organometallic compounds proceed via two competing pathways—the usual nucleophilic and/or thiophilic addition.[11]

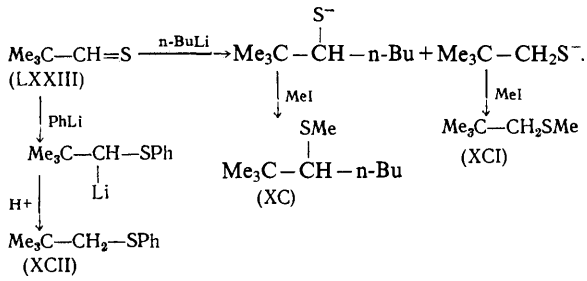
In their study of the interaction of TA with n-butyllithium, Wilson and co-workers observed four types of reactions: C-addition, S-addition, double addition, and reduction.[76] The ratios of the products depend on the structure of the substrate, the solvent, and temperature. For example, $CH_3(CH_2)_4{-}CH{=}S$ reacts with a fourfold excess of n-BuLi in ether at 25 °C to form 73% of the thiol (LXXXVI), 19% of the sulphide (LXXXVII), and insignificant amounts (3 and 4%) of compounds (LXXXVIII) and (LXXXIX). At 0 °C, the yield of compound (LXXXVI) falls to 17%, while in tetrahydrofuran it falls to 2%.



(LXXXVI) (LXXXIX) (LXXXVIII) (LXXXVII)

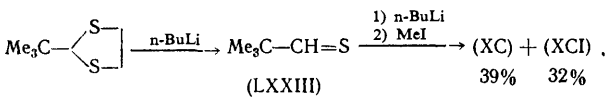
$R = CH_3(CH_2)_4$, $CH_3(CH_2)_5$.

2,2-Dimethylpropanethial (LXXIII) reacts in ether with n-BuLi to form an adduct via the carbon atom and a reduction product.[72] The formation of compounds (XC) (70%) and (XCI) (17%) after the addition of methyl iodide to the reaction mixture is convincing proof of the operation of the reaction pathways illustrated in the scheme.



(LXXIII) (XC) (XCI) (XCII)

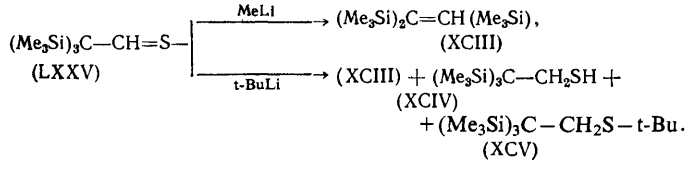
The reaction of 2-t-butyl-1,3-dithiolan with n-BuLi has been achieved[72] by Wilson's method.[76] The formation of the products (XC) and (XCI) in both cases indicates the involvement of the same TA (LXXIII) in the reactions.



(LXXIII) (XC) 39% (XCI) 32%

The TA (LXXIII) reacts with phenyllithium via a thiophilic mechanism with formation of neopentyl phenyl sulphide (XCII) (30%).[65]

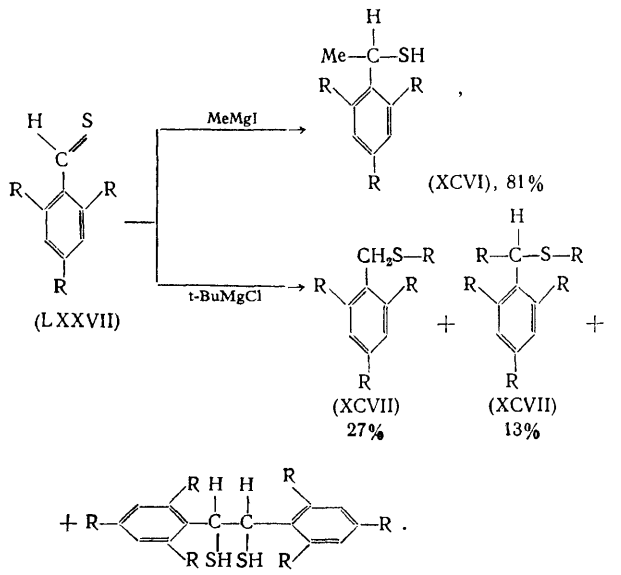
Treatment of tris(trimethylsilyl)ethanethial (LXXV) with methyl- or t-butyl-lithium leads to the alkene (XCIII) in 79 and 34% yields respectively.[17] The thiol (XCIV) (35%) and the sulphide (XCV) (10%) are also formed in the latter case.



(LXXV) (XCIII) (XCIV) (XCV)

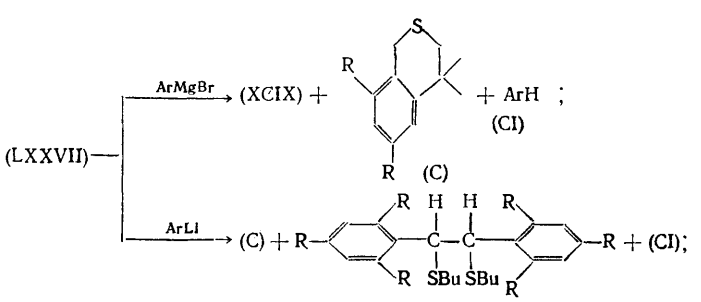
The TA (LXXV) react with a Grignard reagent similarly but at a much lower rate.[17]

Interesting results have been obtained in the study of the reactions of the stable (2,4,6-tri-t-butyl)thiobenzaldehyde (LXXVII) with Grignard and organolithium reagents.[77] The interaction of the thial (LXXVII) with methylmagnesium iodide affords the thiol (XCVI), while the reaction with t-butylmagnesium chloride gives rise to three products: the sulphides (XCVII) and (XCVIII) and the α-dithiol (XCIX).



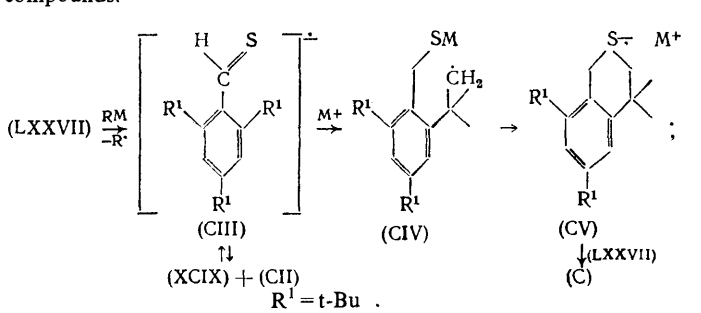
R = t-Bu (XCIX), 31%

In the reactions with the very bulky 2,4,6-tri-t-butyl-substituted phenylmagnesium bromide or phenyllithium, the adducts formed via the carbon or sulphur atom were not detected.[77]



Ar = 2,4,6-(t-Bu)$_3$C$_6$H$_2$; R = t-Bu.

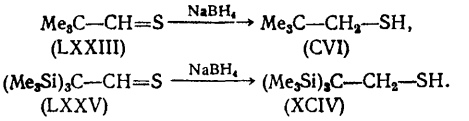
In order to account for the course of the reactions investigated, the authors resorted to the one-electron transfer mechanism[77] used at one time for the reactions of thioketones with organometallic compounds.[11]



R^1 = t-Bu.

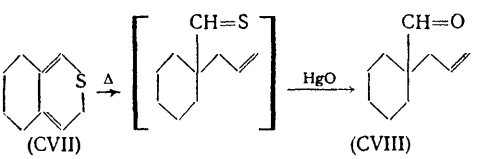
The key intermediate in the proposed scheme is the radical-anion (CIII). Its transformation via the pathway (CIII) → (CIV) → (CV) leads to compound (C), while its dimerisation affords the products (XCIX) and (CII). One should note especially that this is the first example of the dimerisation of thioketyl radicals and the first observation of the generation of a radical-anion from a TA.[77]

Like thioketones, thioaldehydes are readily reduced by the usual reductants to the corresponding thiols. Thus, treatment of 2,2-dimethylpropanethial (LXXIII) with sodium tetrahydroborate gives rise to the neopentanethiol (CVI);[65,72] tris(trimethylsilyl)-ethanethial (LXXV) is transformed quantitatively into the thiol (XCIV).[17] The reactions of TA with alkyl(aryl)lithium reagents or Grignard reagents are accompanied by reduction.[17,65,72,77]

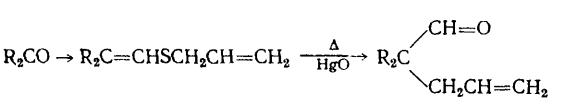


The tendency of TA to oxidise in the presence of atmospheric oxygen has been noted.[39–42] Even the extremely stable t-butyl-substituted thiobenzaldehyde (LXXVII) is converted into the corresponding aldehyde on treatment with oxygen.[16]

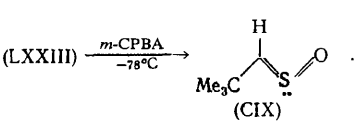
The oxidation of TA *in situ* is of interest for the determination of the reaction mechanism and for preparative purposes. Thus, whereas simple heating of the sulphide (CVII) at 160–180 °C leads to polymeric products, in the presence of red mercury oxide the aldehyde (CVIII) has been obtained in 82% yield.[78]



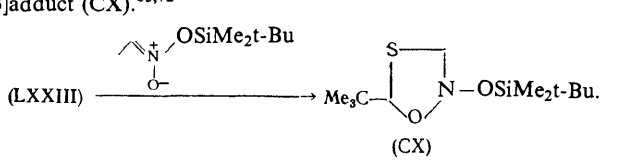
This procedure expands significantly the applicability of the thio-Claisen rearrangement and permits its employment for the synthesis of unsaturated aldehydes from carbonyl compounds.[78]



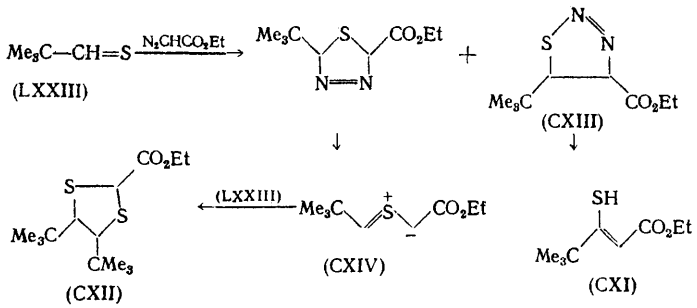
The oxidation of the TA (LXXIII) with *m*-chloroperbenzoic acid (*m*-CPBA) at a low temperature leads to the sulphine (CIX).[65,72]



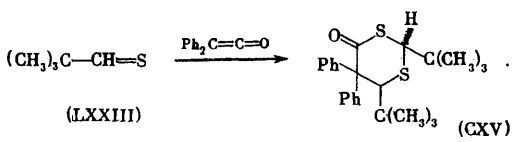
A distinctive feature of thiocarbonyl compounds is their ability to enter into 1,3-dipolar cycloaddition reactions with formation of valuable heterocyclic compounds.[11] In TA, this property is particularly marked and it has been used successfully to trap TA *in situ*.[22,72] Thus, 2,2-dimethylpropanethial (LXXIII) reacts instantaneously with the nitronate ester and affords the cyclic [2 + 3]adduct (CX).[65,72]



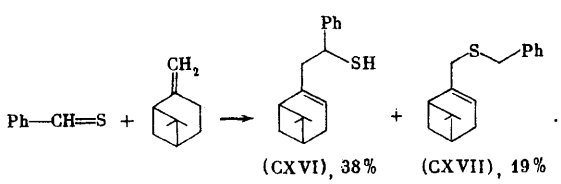
Thiocarbonyl compounds react with diazoalkanes to form the regioisomeric cyclic [2+3]adducts.[11] After the interaction of 2,2-dimethylpropanethial (LXXIII) with ethyl diazoacetate, the thiol (CXI) and an inseparable mixture of the diastereoisomers of compound (CXII) were obtained in equal amounts. The formation of compound (CXI) has been explained by the S–N heterolysis of the thiadiazoline (CXIII) formed initially and subsequent hydride transfer. The dithiolan (CXII) is formed via the thiocarbonyl ylide (CXIV).[65]



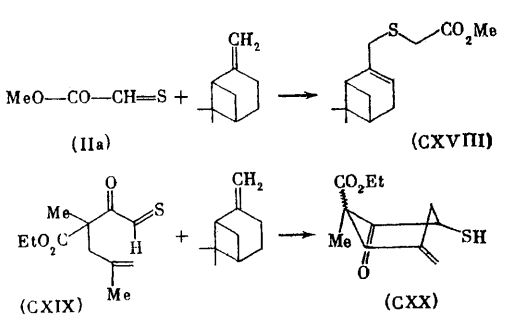
The reaction of the TA (LXXIII) with diphenylketen affords a mixture of 2:1 cyclic adducts (CXV) in a moderate yield. The reaction with dimethylketen or 1,1-diphenylallene do not occur.[72]



Thiobenzaldehyde is capable of participating as a 2π-component in the reaction involving addition to the double bond of β-pinene.[55] The formation of two adducts (CXVI) and (CXVII) is due to the different modes of addition.



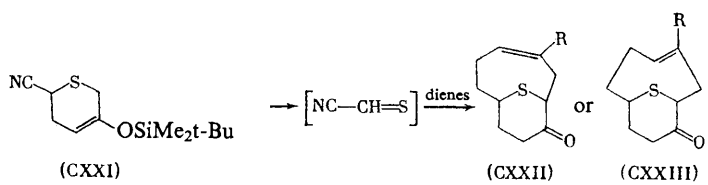
The photochemically generated TA (IIa) reacts with β-pinene at 20 °C to form the sulphide (CXVIII), while the TA (CXIX) affords the substituted cyclohexanone (CXX).[79]



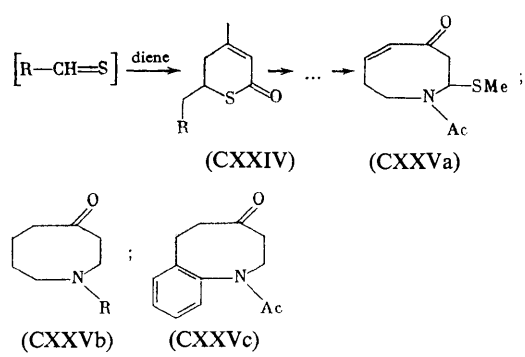
The reactions involving the "ene-inclusion" of TA are evidently promising for the synthesis of cyclic structures under mild conditions. The reactions of TA having electron donor or electron acceptor substituents, generated in different ways, with a wide variety of dienes were examined in detail in Sections III–V. Here it is useful to note studies specially devoted to the cycloaddition reactions of TA.

The characteristic features of the behaviour of thiobenzaldehyde, thioacetaldehyde, and certain other TA in reactions with 2,3-dimethylbutadiene (2,3-DMBD), anthracene, and 9,10-dimethylanthracene have been investigated in detail.[55] It has been found that benzene and toluene are the most suitable solvents, while DMF reduce the yield of the adduct. Appreciable attention has been devoted to the regiochemistry of the cycloaddition reactions and to its relation with the nature of the substituent in TA.[22,61] The dihydrothiopyrans obtained from TA in accordance with Diels–Alder principle can play an important role in the synthesis of natural products, especially of the juvenile hormone, erythronolides, analogues of zygosporin, etc.[61]

The adduct of cyanothioformaldehyde with 2-(t-butyldimethylsiloxy)buta-1,3-diene (CXXI) served as the starting compound for the recently developed synthesis of sulphur-containing bridged cyclodecenones (CXXII) and (CXXIII), which are otherwise difficult to obtain.[80]

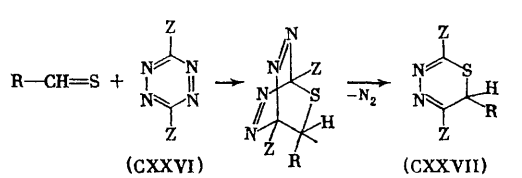


Several methods of synthesis of azocine derivatives (CXXV) have been developed from nitrogen-containing cyclic adducts (CXXIV).[81]



R = $NHCO_2t$-Bu, CH_2NHCO_2t-Bu, $CH_2N(Me)CO_2t$-Bu.

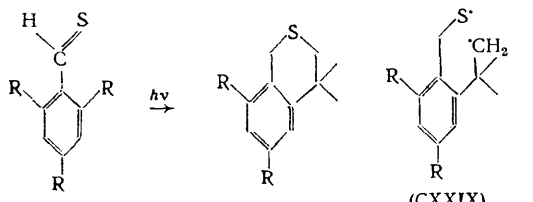
TA with electron-dontaing substituents—thioformates, thioformamides, and thiobenzaldehyde—behave as heterodienophiles in the reaction with tetrazine (CXXVI).[82] The thiadiazones (CXXVII), obtained as a result of the [4+2]cycloaddition, can lose the sulphur atom and can be converted into pharmacologically interesting pyrazoles.



R = OEt, OPr, $N(CH_3)_2$, $N(CH_2)_4O$, $N(CH_2)_5$, Ph.

The unusual properties of the excited thiocarbonyl functional group have been responsible for the development of the photochemistry of thiocarbonyl compounds.[11] The irradiation of a

benzene solution of (2,4,6-tri-t-butyl)thiobenzaldehyde (LXXVII) solution by light from a mercury or sodium lamp ($\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ excitation respectively) leads to the benzothiolan derivative (CX) in 91 or 96% yield respectively.[83] The photochemical formation of the heterocycle (CX) is in this instance unexpected, since the known photochemical reactions of aromatic thioketone containing δ-hydrogen atoms afford cyclopentanethiol derivatives.[11] The occurrence of δ-cyclisation via $n \rightarrow \pi^*$ excitation is also of special interest; in aromatic thioketones, this process takes place via the $S_2(\pi \rightarrow \pi^*)$ state.[11]

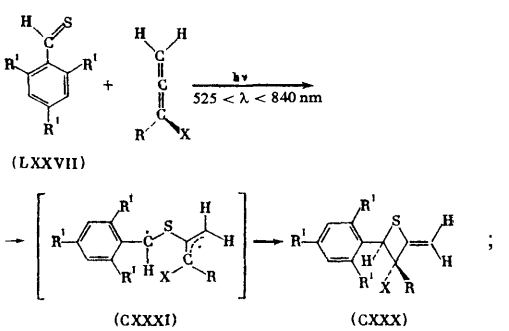


(LXXVII) (C) (CXXIX)

R = t-Bu.

A choice between the possible mechanisms of this reaction—the concerted [2+2]reaction or radical cyclisation via the biradical (CXXIX)—has not so far been made.[83]

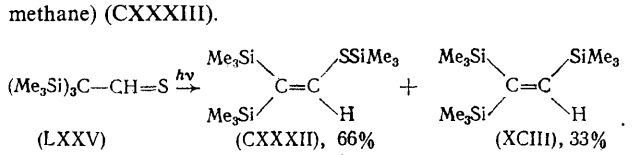
The photochemical reaction of the TA (LXXVII) with unsaturated cumulated systems has been investigated.[84] Irradiation of the TA (LXXVII) jointly with alkoxy-, alkylthio-, or phenylallenes led to a single stereoisomer, namely the thietan (CXXX), via the intermediate biradical (CXXXI).[84]



(LXXVII) (CXXXI) (CXXX)

R = t-Bu.

The photolysis of tris(trimethylsilyl)ethanethial (LXXV) affords two compounds—the substituted sulphide (CXXXII) and the substituted ethene (XCIII).[17] Irradiation of the corresponding aldehyde under analogous conditions led to tris(trimethylsilylmethane) (CXXXIII).

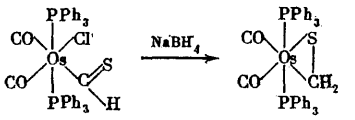


(LXXV) (CXXXII), 66% (XCIII), 33%

$(Me_3Si)_3C-CH=O \xrightarrow{h\nu} (Me_3Si)_3CH.$ (CXXXIII)

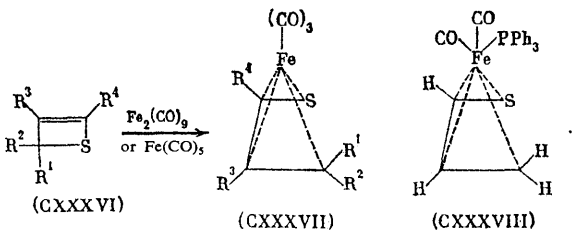
The formation of compound (CXXXII) from the TA (LXXV) via the 1,2-shift of the $SiMe_3$ group from the α-position to the thiocarbonyl carbon atom with the accompanying desulphurisation constitutes a new type of photochemical reaction of thiocarbonyl compounds.[17]

The ability of thioformyl compounds to form complexes with transition metals has been used successfully to detect short-lived TA. The first stable crystalline complex (CXXXIV) of thioformaldehyde has been obtained by the reaction of the unstable thioformyl derivative (CXXXV) with sodium tetrahydroborate.[85]



(CXXXV) (CXXXVI)

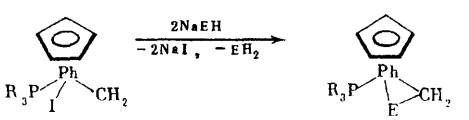
Complexes of the unstable thioacrolein (CXXXVII) have been obtained as red or orange crystals or oils by heating the thiets (CXXXVI) with iron nonacarbonyl or by treating them with iron pentacarbonyl and irradiating.[86] The structure of the complexes (CXXXVII) was established by the X-ray diffraction of the triphenylphosphine derivative (CXXXVIII) formed from compound (CXXXVII) by substituting one of the carbonyl groups by the PPh_3 ligand. The ^1H NMR spectra of the complexes (CXXXVII) have been compared with the spectrum of the molybdenum complex of acrolein.[86]



(CXXXVI) (CXXXVII) (CXXXVIII)

Rhodium complexes of thioformaldehyde and its chalcogen analogues have been obtained recently.[87] The first data are already available on selenoformaldehyde,[88] while telluroformaldehyde is so far unknown.

Compound (CXXXIX) reacts at room temperature in tetrahydrofuran with sodium hydrogen sulphide to form the thioformaldehyde complex (CXLa) in 50% yield. Treatment with NaSeH or NaTeH afforded similarly the complexes of selenoformaldehyde (CXLb) and telluroformaldehyde (CXLc).[87]



(CXXXIX) (CXL)

E = S (a), Se (b), Te (c).

- - - o0o - - -

The fluorine-containing aliphatic TA (CXLI) are formed in the reactions of trialkyl phosphorothionates with ω-hydroperfluoroaldehydes (CXLII) on heating the reactants at 80 °C for 3 h.[89] The ^1H NMR spectrum of the reaction mixture shows a signal at δ = 10.35 p.p.m., which refers to the proton of the monomeric form of the TA (CXLIa), whose content is about 10%. The TA (CXLI) persist in solution at 20 °C for a long time. They react with 2,3-DMBD and isoprene to form the corresponding cyclic adducts.

$$\underset{\text{(CXLII)}}{H(CF_2)_nCH=O} + (RO)_3P=S \rightarrow \underset{\text{(CXLI)}}{[H(CF_2)_nCH=S]} + (RO)_3P=O,$$

n = 4 (a), 6 (b).

A selective route to the synthesis of the unstable thiopropynal (CXLIII) involving the vacuum pyrolysis of dipropargyl sulphide has been found.[90]

$$CH{\equiv}CCH_2SCH_2C{\equiv}CH \xrightarrow[-CH_2{=}C{=}CH_2]{750-950\,^{\circ}C,\ 10^{-3}\ torr} CH{\equiv}C{-}CH{=}S.$$

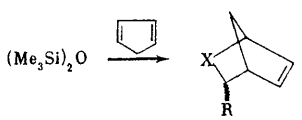
(CXLIII)

The ionisation potential of the TA (CXLIII) is 8.92 ± 0.05 eV and agrees well with the ionisation potentials of other thiocarbonyl compounds.[90] The C=S bond stretching vibration frequency in the IR spectrum of the TA (CXLIII) recorded in an argon matrix at 12 K is about 1100 cm^{-1}.[91]

A new simple method for the direct conversion of aldehydes into thio- and seleno-aldehydes with the aid of bis(trimethylsilyl)sulphide or selenide (CXLIV) in the presence of a catalytic amount n-butyllithium has been proposed.[92]

$$R{-}CH{=}O + (Me_3Si)_2X \xrightarrow[THF]{n\text{-}BuLi} \left[R{-}CH{=}S\right] +$$

(CXLIV)



X = S, Se
R = Ph, 2-thienyl, n-Pr, t-Bu.

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Advances in the chemistry of sulphenic acid amides

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ABSTRACT. Results of recent investigations in the area of sulphenic acid amides have been systematised and correlated in the review. Reactions of sulphenamides occurring with the generation of anions, radicals and nitrenes have been considered, as well as reactions accompanied by fussion of the S–N bond and oxidation of the sulphur atom.

The bibliography contains 95 references.

Contents

I. Introduction 396
II. Reactions occurring with fission of the N–H bond 396
III. Reactions occurring with fission of the S–N bond 398
IV. Reactions occurring with oxidation of the sulphur atom 400

I. Introduction

The chemistry of sulphenic acid amides began in 1911 with the discovery by Zincke of sulphenic acid chlorides and the study of their reactions with nitrogen-containing compounds.[1] The rapid development of this area of hetero-organic chemistry is explained primarily by the useful properties of representative compounds of this class, which are widely used as pesticides,[2] vulcanising agents,[3] electrolytic additives[4,5] and other valuable reagents used in industry and agriculture. The high lability of the S–N bond in sulphenamides, and also the presence of two centres for reaction (sulphur and nitrogen) make sulphenic acid amides extremely valuable as reagents for the synthesis of sulphides,[6,7] disulphides,[8–11] trisulphides,[12] new types of suphenamides,[13] sulphenic acid esters,[14] sulphinamides[15] and sulphonamides.[16]

The interest displayed in sulphenic acid amides by any investigators caused at one time the appearance of a series of reviews[17–22] which reflected in some degree the progress in the chemistry of sulphenamides in a particular period. In the present review results of recent investigations in the chemistry of sulphenic acid amides are systematised and correlated. In particular, reactions are considered which occur with fission of the N–H bond and generation of anions, radicals and nitrenes and reactions accompanied by fission of the S–N bond and oxidation of the sulphur atom.

II. Reactions occurring with fission of the N–H bond

1. Generation of N-anions

Dissociation of N-substituted sulphenamides containing electron-acceptor groups at the sulphur and nitrogen atoms in polar organic solvents leads to the formation of N-anions of the sulphenamides in the stabilisation of which the sulphur atom and the electron acceptor groups participate:[23–25]

$$RSNHR^1 \rightleftharpoons RS\overset{\ominus}{N}R^1 + H^{\oplus},$$
$$RS\overset{\ominus}{N}R^1 \leftrightarrow R\overset{\ominus}{S}{=}NR^1.$$

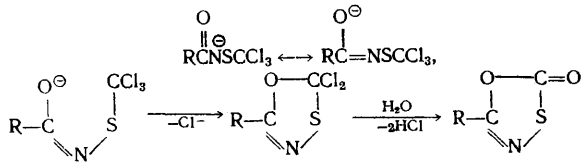
Table 1. pK_a values of N-substituted sulphenamides[25] $RSNHR^1$.

R	R^1	pK_a	Method of determination
C_6H_5	$C_6H_5SO_2$	11.87	a
4-$CH_3C_6H_4$	$C_6H_5SO_2$	12.66	a
4-ClC_6H_4	$C_6H_5SO_2$	10.80	a
4-$NO_2C_6H_4$	$C_6H_5SO_2$	8.20	a
2-$NO_2C_6H_4$	$C_6H_5SO_2$	8.45	a
2,4-$(NO_2)_2C_6H_3$	$C_6H_5SO_2$	5.76	a
2,4-$(NO_2)_2C_6H_3$	4-$CH_3OC_6H_4SO_2$	6.08	a
2,4-$(NO_2)_2C_6H_3$	4-$CH_3C_6H_4SO_2$	5.98	a
2,4-$(NO_2)_2C_6H_3$	4-$ClC_6H_4SO_2$	5.33	a
2,4-$(NO_2)_2C_6H_3$	4-$BrC_6H_4SO_2$	5.31	a
2,4-$(NO_2)_2C_6H_3$	3-$NO_2C_6H_4SO_2$	4.62	a
2,4,6-$(NO_2)_3C_6H_2$	$C_6H_5SO_2$	2.69	a
2,4,6-$(NO_2)_3C_6H_2$	4-$CH_3C_6H_4SO_2$	2.90	a
2,4,6-$(NO_2)_3C_6H_2$	4-$ClC_6H_4SO_2$	2.44	a
3,4,5-$(NO_2)_3C_6H_2$	4-$ClC_6H_4SO_2$	2.88	a
C_6H_5	C_6H_5CO	12.30	a
4-$NO_2C_6H_4$	C_6H_5CO	9.60	a
2-$NO_2C_6H_4$	C_6H_5CO	10.40	a
4-$NO_2C_6H_4$	CH_3CO	10.78	a
2-$NO_2C_6H_4$	CH_3CO	11.38	a
2,4-$(NO_2)_2C_6H_3$	CH_3CO	9.67	a
CCl_3	C_6H_5CO	7.64	b
CCl_3	4-$CH_3C_6H_4CO$	7.67	b
CCl_3	4-$CH_3OC_6H_4CO$	7.69	b

Note. a, potentiometric titration in 50% acetone; b, indicator buffer-free method in acetone.

The stability of the N-anions formed in the dissociation process was determined by the pK_a of sulphenamides (Table 1) the magnitude of which varied over a wide range depending on sulphenamide structure.

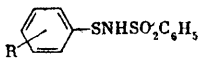
Anions of N-acyltrichloromethanesulphenamides are converted in the presence of base into 5-aryl-1,3,4-oxathiazol-2-ones,[24] which limits the choice of method for determining the pK_a of these compounds.



From a comparison of the pK_a values of N-acyltrichloromethanesulphenamides and the pK_a of dichloroacetic acid (2.70) determined by the same method,[24] it may be concluded that the anions of N-acyltrichloromethanesulphenamides possess high stability.

The character of the substituent on the arenesulphenyl group of N-arenesulphonylarenesulphenamides exerts a greater influence on the stability of the N-anion than does the character of a substituent on the arenesulphonyl group. This is linked with the greater ability of divalent sulphur in comparison with hexavalent sulphur to transmit the inductive influence of the substituent. This situation is also confirmed by correlation analysis, specifically by a comparison of the reaction constants ρ_1 and ρ_2 obtained from the correlation relationships between the pK_a values of two series of N-arenesulphonylarenesulphenamides and the Hammett σ constants (Tables 2, 3).

Table 2. Correlation parameters of a reaction series of N-benzenesulphonylarenesulphenamides.[25]

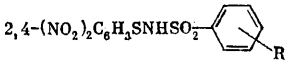


R	pK_a	σ	ρ_1	r
4-NO_2	8.20	0.232	4.717	0.999
4-Cl	10.80	0.227		
H	11.87	0.000		
4-CH_3	12.86	−0.170		

The maximum in the 380–420 nm region in the electronic spectra of solutions of N-arenesulphonylarenesulphenamides corresponds to the absorption of N-anions and is absent from the spectra of N-arenesulphonylalkylarenesulphenamides. An increase in absorption maximum was observed with increase in the acidic properties of N-arenesulphonylarenesulphenamides and also with increase in solvent polarity.[25]

The generation of anions from N-acyl- and N-arenesulphonylarenesulphenamides may be affected by the action on them of alkali or alcoholates.[25] The stability of the resulting sodium salts is caused by the acidic properties of sulphenamides. The sodium salts of N-arenesulphonylnitrobenzenesulphenamides are converted during a few minutes in air to a dark wine-red resin dissolving readily in water with the formation of dark red solutions. The sodium salts of N-arenesulphonyldinitrobenzenesulphenamides are more stable towards the action of moisture and remain unchanged for an extended time.

Table 3. Correlation parameters of a reaction series of N-arenesulphonyl-2,4-dinitrobenzenesulphenamides.[25]



R	pK_a	σ	ρ_2	r
3-NO_2	4.62	0.710	1.537	0.997
4-Br	5.31	0.232		
4-Cl	5.33	0.227		
H	5.76	0.000		
4-CH_3	5.98	−0.170		
4-CH_3O	6.08	−0.268		

In alcoholic solution the sodium salts of N-arenesulphonylarenesulphenamides are methylated at the nitrogen atom by methyl iodide with the formaiton of N-arenesulphonylmethylarenesulphenamides.

2. Generation of N-radicals

Homolysis of the N–H bond in sulphenamides by the action of oxidising agents was noticed for the first time by Lecher and co-workers.[26] They established that under the action of PbO_2 on bis-(benzenesulphenyl)imide in an inert organic solvent the bis-(benzenesulphenyl)imine radical is formed in the stabilisation of which the sulphur atom participates:

$$\cdot\,\mathrm{PhS\!-\!N\!-\!SPh} \leftrightarrow \mathrm{PhS{=}N\!-\!SPh} \leftrightarrow \mathrm{PhS\!-\!N{=}SPh}$$

The action of PbO_2 or (tert.-BuO)$_2$ on N-arenesulphenamides in an inert organic solvent leads to the generation of N-arenesulphenylarylaminyl radicals Ar–SN–Ar^1 (Ar is Ph, 2-$NO_2C_6H_4$, 4-ClC_6H_3; Ar^1 is $MeOC_6H_4$, 4-$(Me)_2(NC_6H_4)$, having as a rule a red colour.[18,26–28]

It was established by EPR[29] that radicals RSNS(Ar) = NSR, coloured blue, green or brown depending on the structure of R and Ar, are formed on oxidation of sulphenamides RSNHC(Ar) = NSR with lead dioxide or silver oxide in diethyl ether in the presence of potassium carbonate.

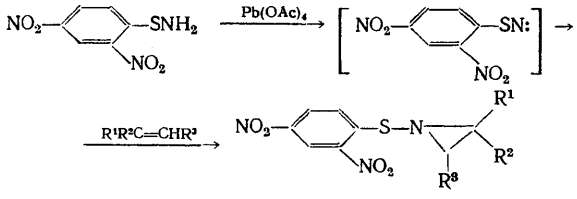
The formation of N-arenesulphenylacylaminyl radicals has been observed[30–33] on heating N-arylsulphenyl-N,N′-bis-(acyl)-arenesulphinamidines in inert organic solvents (benzene, toluene, etc.).

$$\mathrm{ArS(=NAc)N(SAr)Ac} \overset{70\text{–}80^\circ\mathrm{C}}{\rightleftharpoons} 2\mathrm{ArS\dot{N}Ac},$$
$$\mathrm{Ac} = \mathrm{ArSO_2},\ \mathrm{ArCO}.$$

At 120–140 °C the homolysis became irreversible.

3. Generation of nitrenes

The oxidation of 2,4-dinitrobenzenesulphenamide with lead tetraacetate in aprotic organic solvents leads to 2,4-dinitrobenzenesulphenylnitrene which forms the corresponding aziridines with olefins:[34–36]



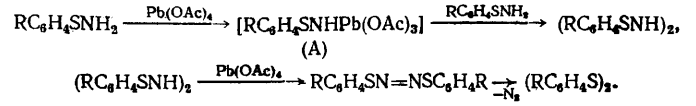
The capture of 2,4-dinitrobenzenesulphenylnitrene by olefins and not by the sulfenamide as in the case of sulphides[37] is explained by the fact that the 2,4-dinitrophenyl group reduces the electron density at the sulphur atom as a result of which the sulphur atom is not capable of undergoing electrophilic attack by 2,4-dinitrobenzenesulphenylnitrene.

In the absence of olefins the oxidation of 2,4-dinitrobenzenesulphenamide by lead tetraacetate leads to N-(2,4-dinitrophenyl)-2,4,dinitrobenzenesulphenamide, which in the opinion of the authors[35] is formed by attack of the nitrene at the nitrogen or sulphur atoms of 2,4-dinitrobenzenesulphenamide. The formation of N,N′-di-[2,4,6-tri-(tert.-butyl)benzene]diiminosulphur in the reaction of 2,4,6-tri-(tert.-butyl)benzenesulphenamide with lead tetraacetate,[38] is also explained by attack of the nitrene at the sulphur atom of the sulphenylamide.

Oxidation of 2,4-dinitrobenzenesulphenamide with lead tetraacetate in the presence of (*Z*)-phenylpropene[34,36] leads to a mixture of trans- and cis-1-(2,4-dinitrobenzenesulphenyl)-2-methyl-3-phenylaziridines, the ratio of which depends on the type of solvent used, the ratio of reactants, and also the order of mixing the reagents. In benzene the ratio of trans- and cis-isomers is 1 : 1, but in chloroform and in methylene chloride it is 3 : 1. In more polar solvents (CH_3CN, CH_3OH) the overall yield of both isomers is reduced. On introducing lead tetraacetate into a mixture of 2,4-dinitrobenzenesulphenamide and (*Z*)-phenylpropene, together with aziridine the formation is observed of N-(2,4-dinitrophenyl)-2,4-dinitrobenzenesulphenamide and partial isomerisation of (*Z*)-phenylpropene into (*E*)-phenylpropene, while addition of a mixture of 2,4-dinitrobenzenesulphenamide and lead tetraacetate in chloroform to (*Z*)-phenylpropene leads to the formation in high yield of only aziridine.

It has been assumed[34] that triplet nitrene is formed initially in the oxidation. This is in equilibrium with singlet nitrene and they both react with (*Z*)-phenylpropane. Since sulphides are effective traps for singlet nitrenes[39] then introduction of sulphide $4\text{-}ClC_6H_4.SCH_2CH=CH_2$ into the reaction mixture changes both the overall yield of aziridines and the ratio of isomers. At the same time in the presence of effective trapping agents for triplet nitrenes $PhC(R)=CH_2$ (R = Ph, Me) the ratio of cis- and trans-isomers is unchanged although the overall yield of aziridines is reduced.

When sulphenamides $RC_6H_4SNH_2$ (R = 2-NO_2, 4-NO_2, 4-Cl) are oxidised with lead tetraacetate in the presence of olefins the corresponding disulphides are isolated. These are formed as a result of the following conversions:[40]



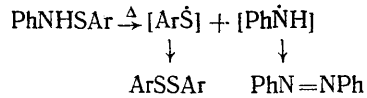
The formation of the nitrenoid intermediate (A) was confirmed by the fact that on oxidation of 4-nitrobenzenesulphenamide with lead tetraacetate in DMSO, N-4-nitrobenzenesulphenyldimethylsulphoximide was obtained.[40]

III. Reactions proceeding with fission of the S–N bond

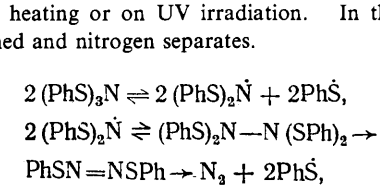
In contrast to the sulphur–nitrogen bond in sulphonamides, which is very stable, the S–N bond in sulphenamides is labile and is readily split by nucleophilic and electrophilic reagents. This was even mentioned by Zincke and co-workers[41] when studying the reaction of naphthalenesulphenyl chlorides with naphthylamines. The stability of S–N bonds in sulphenamides towards nucleophilic and electrophilic reagents is in direct relationship to their bond energies on which there are no data in the literature. This gap is compensated to some extent by data on the order of the S–N bond and force constants. From a study of the vibrational spectra of sulphenamides it was established that the bond order of S–N in N-methyl- and N,N-dimethylsulphenamides is greater than unity,[3] but the force constants of the stretching vibrations of this bond in bis-(arenesulphenyl)imides, N-acyl- and N-arenesulphonylarenesulphenamides are $1894.7-2024.9 \times 10^{-17}$ J.mol.m^2.[42]

1. Homolytic fission of the S–N bond

Homolytic fission of the S–N bond of sulphenamides is as a rule observed on heating or on UV irradiation. For example heating N-phenylarenesulphenamides to 195 °C[43] leads to the formation of the corresponding disulphides and azobenzene which is explained by homolysis of the S–N bond and subsequent dimerisation of the resulting radicals:



The thermal stability of sulphenamides is reduced with increase in their basicity, which occurs in the presence of electron donating substituents bound to the sulphur and nitrogen atoms.[44] Thus homolysis of the S–N bond in tribenzenesulphenamide[45] occurs on mild heating or on UV irradiation. In this case the disulphide is formed and nitrogen separates.



The ease of homolysis of the S–N bond in the given case is explained by the increased stability of the dibenzenesulphenylaminyl radical in the stabilisation of which the sulphur atom participates. In support of this case tristrifluoromethanesulphenylamide is also inclined to photolyse.[46]

$$(CF_3S)_3N + (CF_3S)_2NMe \xrightarrow{h\nu} (CF_3S)_2NH + CF_3SSCF_3 + \\ + (CF_3S)_2NCH_2NHSCF_3.$$

Stable free radicals RSNC(Ar) = NSR are formed on photolysis of sulphenamides $(RS_2)NC(Ar) = NSR$ in aprotic organic solvents.[29] It is not excluded that thermal rearrangement of sulphenamides $4\text{-}RC_6H_4N(R^1)SC = CR^2$ with the formation of derivatives of indole[47] is also effected after homolysis of the S–N bond.

2. Heterolytic fission of the S–N bond

Heterolysis of the S–N bond in sulphenamides occurs under the action of both electrophilic and nucleophilic reagents which are frequently used for synthetic purposes. The reactions of sulphenamides with hydrogen halides, carboxylic and sulphonic acid chlorides and with isocyanates have been well studied and proceed according to the general scheme.[3]

$$RSNHR^1 + X^{\delta+} - Y^{\delta-} \rightarrow \left[\begin{array}{c} \overset{\oplus}{R}SNHR^1 - Y^{\ominus} \\ | \\ X \end{array} \right] \rightarrow RSY + R^1NHX,$$

$XY = HCl,\ TsCl,\ AcCl,\ PhNCO.$

Nucleophilic substitution at the sulphur atom of the amide group is also widely used in various syntheses. Thus reactions of sulphenamides with dialkyl phosphites,[48] thiols,[49] thiocarboxylic acids,[50] and compounds containing active methylene groups[51] are used for obtaining O,O′-dialkyl 5-alkyl phosphonothionates, disulphides, bis-(acyl)disulphides and sulphides:

$$R^1SN(R^2)R^3 + NuH \rightarrow R^1SNu + R^2(R^3)NH,$$
$$NuH = (RO)_2POH,\ RSH,\ RCOSH,\ (NC)_2CH_2,\ (RCO)_2CH_2.$$

When sulphenamides interact with thiol esters of sulphonic acids[52,53] a trans-sulphenylation of the sulphenamide occurs:

$$R^1SN(R^2)R^3 + R^4SO_2SR^5 \rightarrow R^5SN(R^2)R^3 + R^4SO_2SR^1.$$

The reaction is irreversible and takes place only on the interaction of highly nucleophilic sulphenamides (R^2 and R^3 are electron-donating groups) with highly reactive thiol esters of sulphonic acids (R^4 is an electron-accepting group).

Heterolysis of the two S–N bonds in trisulphenamides on interaction with trivalent phosphorus and arsenic compounds leads to the formation of the corresponding imides and disulphides:[54,55]

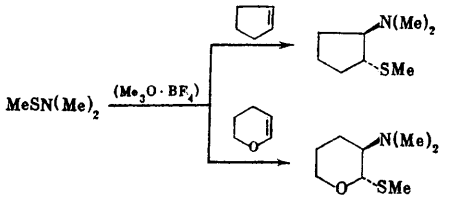
$$Ph_3E + \underset{\underset{R}{|}}{S-N(SR)_2} \rightarrow \underset{\underset{R}{|}}{\overset{\oplus}{Ph_3E}-\overset{\ominus}{S}N(SR)_2} \rightleftharpoons Ph_3E\begin{array}{l} \diagup SR \\ \diagdown N(SR)_2 \end{array} \rightarrow$$

$$\rightarrow Ph_3E{=}NSR + RSSR,$$

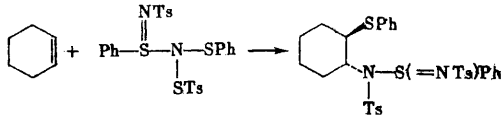
$R = Ph,\ CF_3;\ E = P,\ As.$

At the same time the interaction of *p*-nitrobenzenesulphenamide with triphenylphosphine under the conditions of the Appel reaction proceeds anomalously with splitting of the S–N bond and the formation of the ylide $(p\text{-}NO_2C_6H_4S)_2C{=}P(Ph)_3$.[56]

Heterolytic fission of the S–N bond in the presence of olefins is accompanied by addition of the resulting fragments to the C=C bond of the olefin. For example, heterolytic fission of the S–N bond of N-(dimethyl)methanesulphenamide in nitromethane in the presence of cyclopentene or 3,4-dihydro-2H-pyran leads to the formation of trans-1-dimethylamino-2-methylthiocyclopentane or trans-2-dimethyl-amino-3-methylthiotetrahydropyran.[57,58]

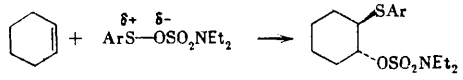


The addition of sulphenamides $PhSNR^1R^2$ [$R^1 + R^2 = (CH)_4$, $R^1 + R^2 = (CH_2)_2O(CH_2)_2$, $R^1 = H$, R^2 = t.-Bu] to the C=C bond of cyclohexene, octene and indene[59,60] also occurs predominantly at the trans-position. Strong proton acids or Lewis acids are catalysts of the aminosulphenylation of olefins. Under conditions of acid catalysis N-benzenesulphenyl-N,N′-bis-(p-toluenesulphonyl)benzenesulphinamidine adds to the C=C bond of cyclohexene with the formation of a benzosulphinamidine trisubstituted at the nitrogen atom.[61]

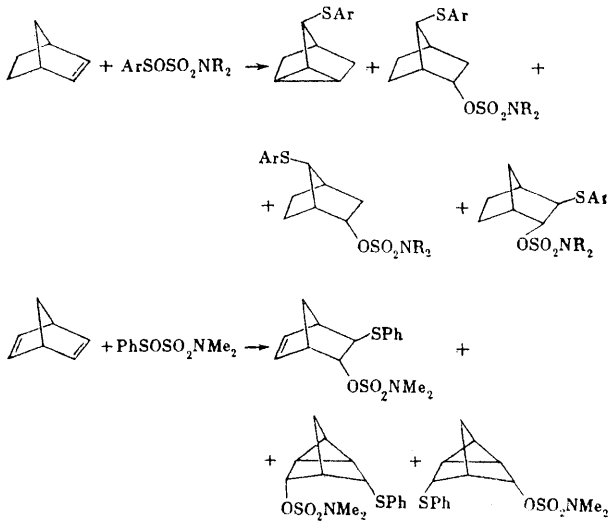


The reactivity of sulphenamides towards olefins in the heterolytic addition reaction increases with an increase in the electrophilicity of the sulphur atom which may be achieved by inserting SO_3 in the S–N bond of sulphenamides.[62] Using this procedure Zefirov and co-workers[63] carried out for the first time the sulphamatosulphenylation of olefins which comprises the interaction of sulphenamides with SO_3 in an inert solvent at a reduced temperature of −85 °C, with subsequent addition of the insertion products to the C=C bond of olefins. The sulphamatosulphenylation of cyclohexene is stereospecific and leads to the trans-1,2-adduct:

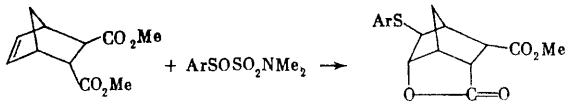
$$ArSNEt_2 + SO_3 \xrightarrow[-\,80^\circ C]{CH_2Cl_2} ArSOSO_2NEt_2$$



The sulphamatosulphenylation of norbornene and norbornadiene[63] is accompanied by rearrangement of the carbon skeleton which finally leads to a mixture of several products:



On sulfamatosulphenylation of bicyclo[2.2.1]hept-2-en-endo-cis-5,6-dicarboxylic acid dimethyl ester cyclisation of the adducts occurs with the formation of arylthiolactones:[63]



The use of pyridine/sulphur trioxide as SO_3 donor[64] makes it possible to carry out this reaction at room temperature. It was shown[65] that the sulphamate group is relatively easily replaced both by weak (CF_3COO^-, $HCOO^-$) and by strong (Br^-) nucleophiles.

IV. Reactions occurring with oxidation of the sulphur atom

Oxidation reactions of the divalent sulphur in sulphenamide to the quadri- and hexavalent state forming sulphin- and sulphonamides have been known and studied for a long time. However a series of reactions has been carried out during which the sulphur in sulphenamides increases its valency by two units and adds an atom of halogen or an imino, alkoxy or amido group. These reactions have become known relatively recently and have still not been studied fully.

1. Oxidative imination of sulphenamides

Conversions accompanied by oxidation of an element and by addition of an imino group are taken to be called oxidative imination reactions.[66]

It has been established[67] that sulphenamides $ArSNRR^1$ (R = H, Alk; R^1 = Alk) react with the sodiochloroamides of arenesulphonic acids according to the general reaction scheme of oxidative imination with the formation of N,N′-substituted amides of iminosulphinic acids:

$$ArSNRR^1 + TsNNaCl \xrightarrow{-NaCl} ArS(=NTs)NRR^1.$$

Sulphenamides ArSNHX [X = C(=NH)NH_2, C(=NH)Alk, C(=NH)SAlk, C(=NH)OAlk] are iminated by sodiochloroamides of sulphonic acids,[67] N-chlorobenzamide,[68] and N-bromobenzamidine.[69] N-Acylsulphenamides p-$NO_2C_6H_4SNHAc$ are iminated in the presence of base by N-chloroacet- and N-chlorobenzamide[70] and also by N-bromobenzamidine.[68] However attempts[67] to effect the imination of N-acyl- and N-arenesulphonylarenesulphenamides with the sodiochloroamides of sulphonic acids in acetone were completed without a result which is explained by the reduced electron density at the sulphur atom of these sulphenamides.

The mechanism of oxidative imination of sulphenamides by N-halogen compounds has not been investigated in detail, however by analogy with the oxidative imination of sulphides[71,72] it has been proposed[73] that the chlorine atom of the N-halogen compound attacks electrophilically the sulphur atom of the sulphenamide with the formation of a chlorosulphonium intermediate which forms an ion pair with the amidate anion:

$$ArSNRR^1 + ClNHR^2 \rightleftharpoons \left[Ar\overset{\oplus}{S}(Cl)NRR^1\overset{\ominus}{N}HR^2 \right] \xrightarrow{-HCl} ArS(=NR^2)NRR^1.$$

The possibility of forming the chlorosulphonium intermediate by electron transfer from the sulphur atom to the positively charged chlorine atom is not excluded.[74] It is evident that the electron density on the sulphur atom must be sufficient for electrophilic attack by chlorine cations. In this connection it seemed of interest to activate the sulphur atom in the oxidative imination reaction by creating an α-N-anionic centre[75] which makes possible the imination of N-substituted sulphenamides containing electron accepting groups on the sulphur and nitrogen atoms. Thus the selection of conditions for imination in the case of N-monosubstituted sulphenamides is determined by their acidic properties.[25] Unionised sulphenamides with $pK_a > 11$[74–76] are iminated in acetone by sodiochloroamides of sulphonic acids:

$$RSNHR^1 + ArSO_2NNaCl \xrightarrow{-NaCl} RS(=NSO_2Ar)NHR^1,$$

R=Ph, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, R^1=H;
R=CH_2Cl, R^1=AlkCO, ArCO; R=Ph, R^1=AlkCO, ArCO; R=Ph, 4-MeC_6H_4, R^1=$ArSO_2$.

Sulphenamides with pK_a 8–11[77,78] are not iminated in acetone but are iminated in strongly basic solvents of high dielectric constant (aqueous alkaline solution, pyridine, etc.) capable of dissociating sulphenamides with the formation of an α-N-anionic centre:

$$RSNHR^1 \rightleftharpoons RS\overset{\ominus}{N}R^1 + H^{\oplus},$$
$$RS\overset{\ominus}{N}R^1 \leftrightarrow R\overset{\ominus}{S}=NR^1.$$

The sodium salts of such sulphenamides are readily iminated by sodiochloramides of sulphonic acids in acetone.

$$\left[RS{=}NR^1 \right]^{\ominus}Na^{\oplus} + ArSO_2NNaCl \xrightarrow{-NaCl} \left[ArSO_2N{=}\underset{R}{S}{=}NR^1 \right]^{\ominus}Na^{\oplus}$$

R=4-$NO_2C_6H_4$, R^1=AlkCO, ArCO
R=4-ClC_6H_4, 2-NOC_6H_4, 4-$NO_2C_6H_4$, R^1=$ArSO_2$.

Sulphenamides with pK_a < 8 [79–82] are iminated in acetone and also in aqueous alkaline medium and in pyridine since the concentration of N-anion is still sufficiently high, however they are not iminated in benzene, toluene, hexane or in solvents of low dielectric constant suppressing the dissociation of the sulphenamide.

$$\left[RS{=}NR^1\right]^{\ominus}H^{\oplus} + ArSO_2NNaCl \xrightarrow[-NaCl]{} \left[ArSO_2N{=}\underset{\underset{R}{|}}{S}{=}NR^1\right]^{\ominus}Na^{\oplus}$$

R=EtOCOCCl$_2$, R^1=ArCO, R=CCl$_3$, R^1=AlkCO, ArCO, ArSO$_2$; R=CFCl$_2$, R^1=AlkCO, ArCO; R=CF$_2$Cl, R^1=AlkCO, ArCO.

Since the formation of sodium salts of sulphenamides occurs first on interacting sulphenamides having pK_a < 6 with sodiochloroamides of sulphonic acids (N-chlorobenzenesulphonamide has pK_a 9.5 [83]), their imination was conducted at a reactant ratio of 1 : 2.[25,80]

$$RSNHSO_2R^1 + ArSO_2NNaCl \xrightarrow[-\left[ArSO_2NHCl\right]]{} \left[RS{=}NSO_2R^1\right]^{\ominus}Na^{\oplus} \xrightarrow{ArSO_2NNaCl} \rightarrow \left[ArSO_2N{=}\underset{\underset{R}{|}}{S}{=}NSO_2R^1\right]^{\ominus}Na^{\oplus}$$

R = 2,4-(NO$_2$)$_2$C$_6$H$_3$, CCl$_3$

The direction of the reaction of N-acyl-p-nitrobenzenesulphenylamides with the sodiochloroamide of sulphonic acids depends on the conditions. Imination of these sulphenamides is effected in aqueous alkaline medium but in pyridine the interaction of these compounds is accompanied by fission of the S–N bond and the formation of symmetrical N,N′-bis-(arenesulphonyl)-p-nitrobenzenesulphinamidines.[78] A similar symmetrisation was also observed[24] in the interaction of N-acylmethanesulphenamides with sodiochloroamides of sulphonic acids in acetone.

$$MeSNHCOR + ArSO_2NNaCl \cdot xH_2O \rightarrow \begin{cases} \rightarrow MeS(=NSO_2Ar)NHCOR \\ \rightarrow MeS(=NSO_2Ar)NHSO_2Ar \end{cases}$$

This process has been studied in more detail in the example of the reaction of sodiochloroamides of sulphonic acids with bis-(arenesulphenyl)imides, the products of which were a mixture of N,N′-bis-(arenesulphonyl)arenesulphinamidines and N-arenesulphonylarenesulphinamidines.[84]

$$ArSNHSAr + 3PhSO_2NNaCl \cdot xH_2O \rightarrow \begin{cases} \rightarrow ArS(=NSO_2Ph)NH_2 \\ \rightarrow Ar(=NSO_2Ph)NHSO_2Ph \end{cases}$$

Ar = 2-NO$_2$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$.

The formation of a mixture of two products is explained by two factors. The first is the low rate of imination of sulphenamides which is determined by the low electron density on the sulphur atom and the impossibility of compensating for it by the formation of an α-N-anionic centre since bis-(arenesulphenyl)imides are relatively weak NH-acids with pK_a 10.8.[84] The second is the lability of the sulphur–nitrogen bond, and its fission in the presence of water of crystallisation with the formation of diaryldisulphides and arenesulphenamides, the further imination of which leads to the formation of the reaction products.

$$ArSNHSAr \rightarrow \begin{cases} \rightarrow ArSNH_2 \\ \rightarrow [ArSOH] \rightarrow 0.4ArSSAr + 0.2ArSO_3H + 0.4H_2O \end{cases}$$

$$ArSNH_2 + PhSO_2NNaCl \rightarrow ArS(=NSO_2Ph)NH_2,$$

$$0.4ArSSAr + PhSO_2NNaCl \rightarrow 0.8ArS(=NSO_2Ph)NHSO_2Ph.$$

Such ideas were confirmed on studying the reaction of bis-(2,4-dinitrobenzenesulphenyl)imide with the sodiochloroamide of benzenesulphonic acid in acetone where the formation of N-benzenesulphonyl-2,4-dinitrobenzenesulphinamidine and of 2,4,2′,4′-tetranitrodiphenyldisulphide was observed. These, as is known[85], are not imidated by the sodiochloroamides of sulphonic acids:

$$[2,4\text{-}(NO_2)_2C_6H_3S]_2NH \xrightarrow{PhSO_2NNaCl \cdot xH_2O} \begin{cases} \rightarrow 2,4\text{-}(NO_2)_2C_6H_3S(=NSO_2Ph)NH_2 \\ \rightarrow [2,4\text{-}(NO_2)_2C_6H_3S-]_2 \end{cases}$$

The imination of N-acyl- and N-arenesulphonylsulphenamides by N-chloroamides of carboxylic acids[68,86] is carried out in the presence of organic bases which play the role not only of acceptors of hydrogen chloride but also are capable of dissociating the initial sulphenamides:

$$\left[RS{=}NAc\right]^{\ominus}H^{\oplus} + R^1CONHCl \xrightarrow[-HCl]{} \left[R^1CON{=}\underset{\underset{R}{|}}{S}{=}NAc\right]^{\ominus}H^{\oplus}$$

2. Oxidative halogenation of sulphenamides

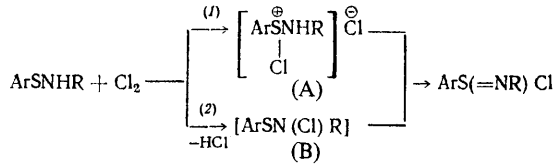
The chlorination of N-substituted sulphenamides by chlorine in non-aqueous aprotic organic solvents leads to the formation of the acid chlorides of N-substituted iminosulphinic acids.[87]

$$ArSNHR + Cl_2 \xrightarrow[-HCl]{} ArS(=NR)Cl,$$

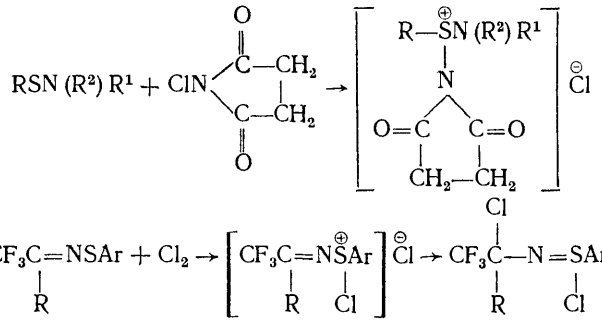
R=ArSO$_2$, ArCO, tert-Bu.

Dichloroamides of sulphonic acids, N-chloroimides, and tert.-butyl hypochlorite are also used as chlorinating agents. The chlorination of weakly nucleophilic sulphenamides is carried out in the presence of organic bases. The susceptibility of sulphenamides to oxidative chlorination is explained by the electron density on the sulphur atom. The presence of electron accepting groups on the sulphur and nitrogen atoms hinders oxidative chlorination or makes it impossible.[87]

The mechanism of the oxidative chlorination of sulphenamides has not been studied in detail. However allowing for the possibility of attack of chlorine cations at both the sulphur atom and the nitrogen atom it has been proposed[87] that the formation of the acid chlorides of iminosulphinic acids may occur by two concurrent schemes (1) and (2).



The most probable of these seems to be Scheme (1) since the intermediate N-chlorosulphenamides (B) [Scheme (2)] do not always succeed in rearranging to acid chlorides of iminosulphinic acids.[87] At the same time the appearance of chlorosulphonium salts of type (A) is recorded in reactions of N,N-dialkylsulphenamides with N-chlorosuccinimide,[88] and also of N-arylsulphenylketimines with chlorine:[89,90]



The hypothesis of a high probability of chlorinating sulphenamides at the sulphur atom is also in agreement with the principle of hard and soft acids and bases.[91] Evidently chlorination at the nitrogen atom is possible only in the event of low electron density at the sulphur atom, i.e. in the presence of strongly electron-accepting groups on the sulphur and nitrogen atoms. Replacement of a hydrogen atom on the nitrogen of N-arenesulphonylarene-sulphenamides by a metal atom increases the reactivity of the latter in oxidative chlorination reactions, which is seemingly explained by the increase in electron density at the sulphur atom as a result of the effects of the α-N-anionic centre:[92]

$$ArSN(Na)SO_2Ph + Cl_2 \rightarrow ArS(=NSO_2Ph)Cl + NaCl.$$

The oxidative chlorination of N,N-di(trifluoromethylsilyl)-trifluoro-methanesulphenamides is accompanied by splitting of the N–Si bond:[93]

$$CF_3SN(SiMe_3)_2 \xrightarrow[-ClSiMe_3]{Cl_2} [CF_3S(=NSiMe_3)Cl] \xrightarrow[-ClSiMe_3]{Cl_2} CF_3S(=NCl)Cl.$$

Only one sulphur atom participates in the oxidative chlorination of bis-(trifluoromethanesulphenyl)imide:[93]

$$(CF_3S)_2NH + Cl_2 \rightarrow CF_3S(=NSCF_3)Cl + HCl.$$

3. Oxidative alkoxylation and amidation of sulphenamides

The increased susceptibility of the sulphur atom of N-substituted sulphenamides to attack by chlorine cations under conditions of generating an α-N-anionic centre makes this method of activating sulphur promising in reactions accompanied by oxidation of the sulphur atom. For example, it has been shown[94] that the sodium salts of N-arenesulphonylarenesulphenamides are very readily chlorinated by tert.-butyl hypochlorite in alcohols (the reaction is exothermic) with the formation of alkyl esters of N-arene-sulphonylareneiminosulphinic acids (oxidative alkoxylation reaction).

$$ArSNHSO_2Ph + \text{tert-BuOCl} \xrightarrow{RONa} ArS(=NSO_2Ph)OR + \text{tert-BuOH} + NaCl,$$
$$R = Me, Et;\ Ar = 2\text{-}NO_2C_6H_4.$$

The chlorination of these salts by chlorine in acetone in the presence of dialkylamines[95] leads to the formation of N,N-dialkyl-N′-arenesulphonylarenesulphinamidines (oxidative amidation reaction).

$$ArSN(Na)SO_2Ph + Cl_2 + 2R_2NH \rightarrow ArS(=NSO_2Ph)NR_2 + NaCl + R_2NH\cdot HCl.$$

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Translated from *Uspekhi Khimii* **59** 705–737 (1990) U.D.C. 547.717

New advances in the chemistry of thiirans

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ABSTRACT. Data concerning the methods of synthesis of thiirans, their reactions with nucleophiles and electrophiles, as well as their desulphurisation and homolytic reactions and their behaviour in cycloaddition reactions are surveyed.

The bibliography includes 285 references.

Contents

I. Introduction 405
II. Methods of synthesis 405
III. Reactivity 411

I. Introduction

Data on thiirans and their derivatives published after 1976 inclusive have been examined in a monograph.[1] Certain new ways of synthesising thiirans have been discussed in a review.[2] L'Abbé's communication[3] is devoted to a new type of thiirans—thiiran imines. Some of the studies published after 1976 have been included in annual publications on three-membered heterocycles[4–8] and in review articles.[9–12] These data reflect fairly completely the state of the chemistry of thiirans by the end of the 1970's but they do not enable one to obtain an idea about the pathways and trends followed in its development during the current decade.

The present review deals with the principal advances in the synthesis and in the study of the properties of thiirans and their derivatives published in the last ten years. The restricted size of the review precluded the inclusion in it of information about the theoretical and physicochemical studies of these substances and about their applications.

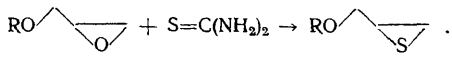
A characteristic feature of the latest studies in the field of thiirans is their increasing applied bias with expansion of the range of their applications. Thus the possibility of synthesising from these compounds of a wide variety of biologically active substances, for example adrenoblocking agents,[13] immunomodulators,[14] antiseptics,[15] antihypertension agents,[16] hypoglycaemic agents,[17] etc., has been demonstrated in recent years. New technical applications of thiirans have been developed: for the preparation of liquid crystals,[18] photoresistors,[19] components of paint and varnish coatings,[20,21] antioxidants,[22,23] thermostable insulating materials,[24] heat-resistant polymers,[25] semiconductors,[26] elastomers,[27] etc.

II. Methods of synthesis

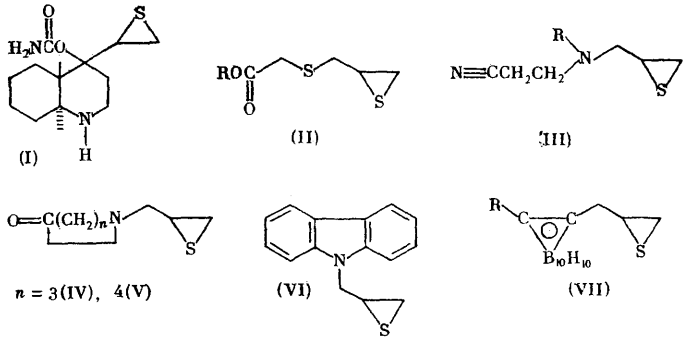
The classical methods of synthesis of thiirans[1] have been the basis of the majority of new synthetic studies in the field. During the past period, there has been an expansion of ideas concerning the effect of conditions on the formation and yield of thiirans in classical reactions, on the limits of their applications, and on the range of precursors of epithio-compounds. Ideas about the mechanisms of the formation of thiiran rings developed earlier have exerted a major influence on the new syntheses of thiirans.[1] By testing them with new models, it has been possible to discover new effective thiolating agents and to develop in a number of instances new non-traditional approaches to the synthesis of thiirans.

1. Conversions of oxirans into thiirans

The reactions of oxirans with thiourea have been used to obtain a large number of new epithio-compounds, including some which had been previously unavailable. With the aid of thiourea, substituted epithioglycidyl ethers containing polychloroalkyl,[28,29] 2-alkoxyethyl,[30] furfuryl,[31] organosilylalkyl, alkenyl, and alkynyl,[32,33] and t-butyl[34] end groups have been obtained.[28–34]

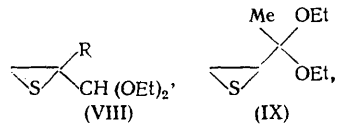


Acid catalysis has been used successfully in a number of instances.[31,34] The selection of the solvent, catalyst, and reaction conditions made it possible to devise simple methods of synthesis of a wide variety of epithioglycidyl ethers.[21,28–34] Many compounds containing the thiiran ring have been obtained by the reaction of thiourea with oxirans: the amide (I),[35] thioglycolic esters (II),[36] cyanoethylated amines (III),[37] the pyrrolidinone (IV) and the piperidinone (V),[38] the carbazole (VI),[39] and the *o*-carbaboranes (VII).[40]

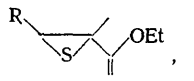


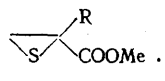
The presence of electron-accepting substituents in the ring of oxirans hinders their reactions with thiourea. The diethylacetals (VIII) have been obtained from the corresponding oxirans only on heating in methanol.[41,42] Acetylthiiran diethylketal (IX) was obtained similarly.[43] The ketals of 2-R-2-acetylthiirans polymerise under these conditions, while 2-R-2-(1-ethoxyvinyl)thiirans (X) are formed in preparative yields.[43] The reactions of sterically hindered

glycidates with thiourea in methanol are catalysed by H_2SO_4, which made it possible to obtain in high yields the thioglycidates (XI), which were previously difficult to synthesise.

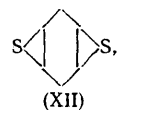

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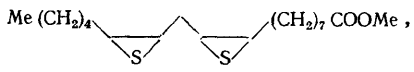
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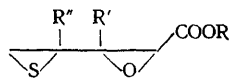

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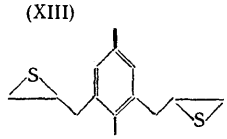

(XI)

Diepithio-compounds have been obtained by the reaction of thiourea with diepoxides. In the presence of H_2SO_4, *cis*- and *trans*-1,4-diepoxycyclohexanes were converted into the corresponding diepithio-compounds (XII).[44] The stereoisomers of the methyl esters of 9,10,12,13-diepithiooctadecanoic acid (XIII) have been synthesised in dioxan (XIII).[45] The sterically hindered esters of 3-substitutes and 3,4-disubstituted 2,3,4,5-diepoxyvaleric acids have been selectively converted in methanol (40 °C, 5–6 h) into the 3,4-epithio-derivative (XIV).[46] 2,5-Di(2,3-epithiopropyl)-1,4-dimethylbenzene (XV) has been obtained under mild conditions.[47]

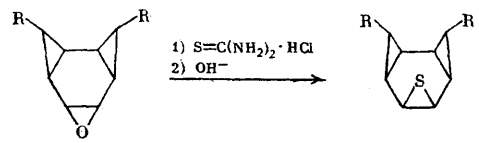

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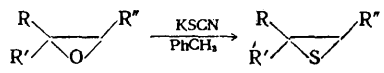

(XIV)


(XV)

Thiourea salts are sometimes used for the thiolation of oxirans. Thus 3,4-epithiothiolan 1,1-dioxide has been obtained by the reaction of 3,4-epoxythiolan 1,1-dioxide with a thiourea salt.[48] *cis*-Thiatris-σ-homobenzenes have been obtained similarly.[49]

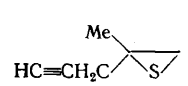


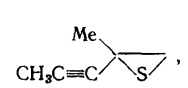
New aspects of the thiolation of oxirans by metal thiocyanates have been less thoroughly investigated. The use of potassium thiocyanate in toluene in the presence of silica gel made it possible to obtain substituted thiirans in 70–90% yield.[50]

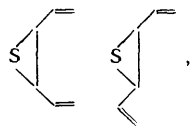


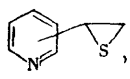
When an attempt was made to increase the rate of thiolation of oxirans by thiocyanates with the aid of a phase transfer catalyst, the yield of thiirans fell appreciably.[51]

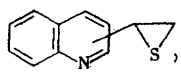
Under the conditions usual for the reactions of oxirans with KSCN, certain new epithio-compounds have been obtained. The thiirans with alkynyl substituents (XVI) and (XVII),[52] and *cis*- and *trans*-divinylthiirans (XVIII)[53] are formed in aqueous alcohol in yields up to 70%, while pyridyl-, quinolinyl-, and isoquinolinyl-thiirans (XIX)–(XXIII) are formed in a yield up to 50%.[54] The epithio-derivatives of limonene (XXIV) and terpinolene (XXV) have been obtained in anhydrous alcohol,[55] while a mixture of *cis*- and *trans*-dideuterio-thiirans have been synthesised in water.[56] Furyl- and thienyl-thiirans (XXVI) have been synthesised in the presence of small amounts of water.[57]

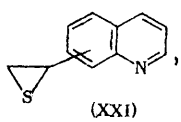

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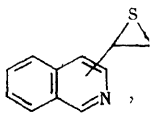

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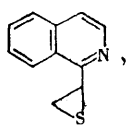

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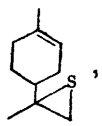

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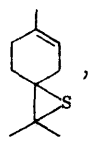

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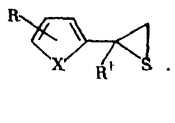

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(XXII)

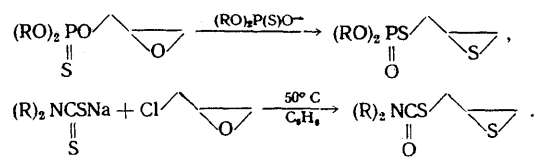

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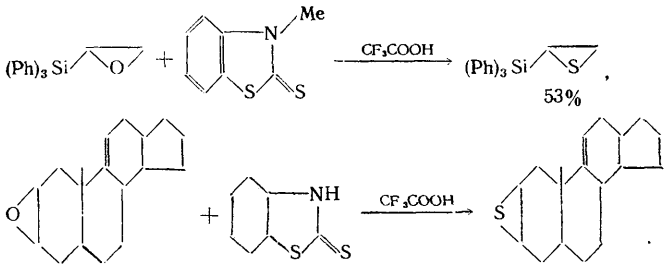

(XXVI)

Thiono-compounds have been used as thiolating agents for the conversion of oxirans into thiirans. Triphenylphosphine sulphide with an equimolar amount of CF_3COOH has been used to synthesise 3,4-epithiothiolan 1,1-dioxide.[58] 10β-Epithiosteroids have been obtained from epoxysteroids and triphenylphosphine sulphide in the presence of picric acid.[59] Ethylene and propylene sulphides are formed on reaction of the corresponding oxirans with the monoesters of alkylphosphonothioic acids.[60] A similar reaction occurs on heating glycidyl phosphorothioates with salts of dialkyl phosphorothioic acids.[61] The salts of dithiocarbamic acid also have similar properties.[62]



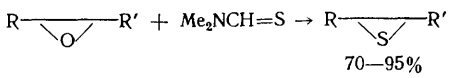
The interaction of triphenylsilyloxiran with an equimolar amount of 3-methylbenzothiazole-2-thione and CF_3COOH afforded the first representative of silylthiirans.[63] Epoxy-compounds are converted

into thiirans under the same conditions on treatment with perhydrobenzothiazole-2-thione.[64]



The thiono-derivatives of triazoline, imidazoline, benzimidazoline, and oxadiazoline thiolate oxirans also in the absence of CF_3COOH, which is indicated by the formation of 1-heteroaryl-2,3-epithiopropanes on interaction of azolethiones with epichlorohydrin.[65,66] Many side processes are ruled out in the presence of CF_3COOH.

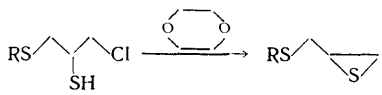
Among thiono-compounds investigated, dimethylthioformamide in the presence of catalytic amounts of CF_3COOH proved to be the most effective.[67]



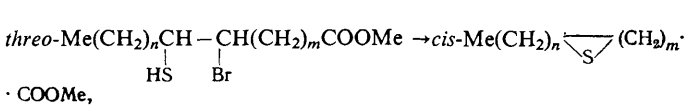
2-Mercaptobenzothiazole[68] and 5-mercapto-1-phenyltetrazole[69] were also found to be highly effective thiolating agents.

2. Cyclisation of 2-substituted thioles and their derivatives

2-Chloroalkanethiol fragments in a polymer matrix are converted into epithioalkyl groups even on solvation with 1,4-dioxan.[70]

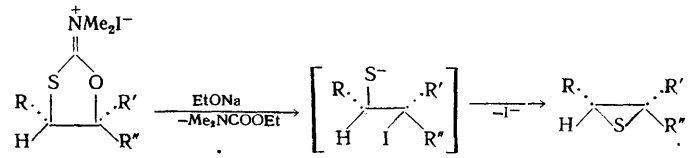


Analogous reactions are characteristic also of monomeric 2-halogenoalkanethiols. Thus the carbaboranylthiirans (VII) are formed rapidly from 3-chloro-2-mercaptopropyl-*o*-carbaboranes on heating in methanol.[71,72] 3-Halogeno-4-mercaptothiolan 1,1-dioxides are spontaneously converted into 3,4-epithiothiolan 1,1-dioxides.[73] In both cases, the formation of a ring is energetically so favourable that its opening by anhydrous HCl either does not occur or takes place to only a slight extent. 2-Chloro-1-trifluoromethylethanethiol is somewhat more stable, but on treatment with *N*-methylpyrrolidinone it is converted into trifluoromethylthiiran already at 20 °C.[74,75] The stereospecificity of the reactions considered, taking place with inversion of configuration has been demonstrated on new examples.[76]



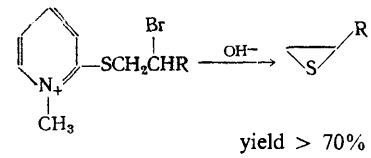
$n = m = 7$; $n = 10$, $m = 4$.

2-Halogenoalkanethiolate ions are precursors of thiirans in many reactions. The interaction of 3,4-dibromo-3-methylbutan-2-one oxime with Na_2S in acetone leads to the oxime of 2-acetyl-2-methylthiiran.[77] The methiodides of 2-methylimino-1,3-oxathiolans are converted into epithio-compounds,[78] apparently in accordance with the mechanism



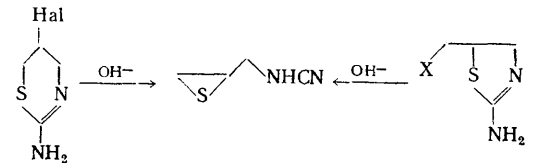
The vicinal alicyclic substituted iodine thiocyanates, including steroids are converted quantitatively into thiirans on treatment with $EtBH_3Li$.[79]

Ethylene sulphide or its polymer are formed from 2-bromoethylisothiuronium bromide[80] and 2R-thiirans are produced from 2-(2-bromoalkylthio)pyridinium salts.[81]

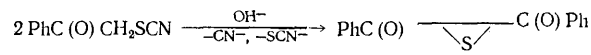


yield > 70%

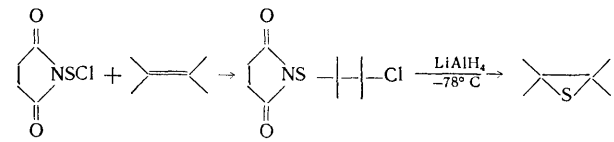
The skeletal rearrangement of cyclic 2-halogenoalkylisothioureas into 2,3-epithiopropylcyanamide can apparently be explained by the formation of 2-halogenoalkanethiolate anions.[82]



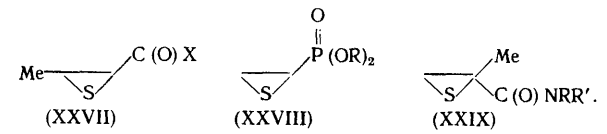
Dibenzoylthiiran is formed from α-thiocyanatoacetophenone on treatment with bases under phase transfer conditions.[83]



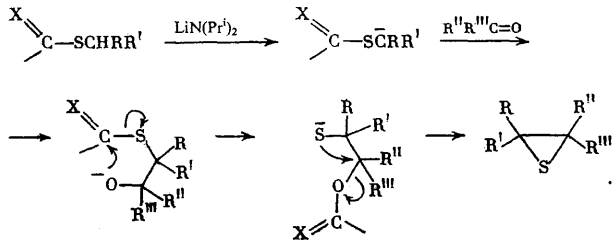
The adducts of *N*-chlorosulphenylated succinimides and phthalimides with alkenes also proved to be precursors of thiirans.[84,85] Their reduction with $LiAlH_4$ makes it possible to obtain thiirans in yields up to 90% and more.



The thiirans (XXVII)–(XXIX), which readily lose the sulphur atom, have been obtained under mild conditions from β-acylthio-α-chloro-derivatives of carboxylic[86] or phosphonic[87] acids and from derivatives of 3-chlorothietan-2-one.[88]

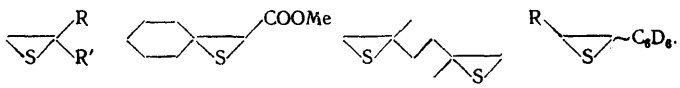


A new aspect of the synthesis of thiirans is based on the reactions of carbonyl compounds with sulphur-containing carbanions in which the sulphur atom is linked to a coordinatively unsaturated carbon atom.[89–94] The intermediate oxy-anions of these compounds rearrange to precursors of thiirans—2-substituted thiolate anions.



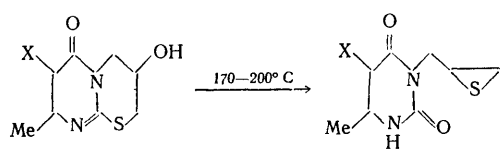
Thio- and dithio-carbonates and 2-alkylthio-1,3-oxazolines have been widely investigated in reactions with carbonyl compounds (aliphatic and aromatic aldehydes and acyclic and alicyclic ketones). The method makes it possible to obtain different thiirans, including optically active thiirans (XXX), substituted thioglycidates (XXXI), bisthiirans (XXXII), etc.

Instead of aldehydes and ketones, it is possible to use alkyl thiolocarboxylates; they acylate sulphur-containing carbanions to α-thiolated ketones, which after reduction afford thiirans, for example, compound (XXXIII), in high yields.[95]



(XXX) (XXXI) (XXXII) (XXXIII)

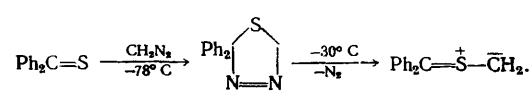
The thermal reactions of 2-hydroxyalkanethiol derivatives, in which the sulphur atom is linked to a coordinatively unsaturated atom, belong to this type. Thus, 2-R-thiirans and (especially readily) 2-R-2-R′-thiirans are formed on thermolysis of 2-hydroxyalkanethiol esters of phosphorus acids.[96] Epithiopropylpyrimidines are formed similarly from 3-hydroxypyrimidothiazines:[97]



trans-2-Bromocyclohexanol is converted into epithiocyclohexane in a similar way on interaction with an excess of KSCN in aqueous alcohol.[98]

3. Homolytic Methods of Synthesis

The biradical mechanism of the formation of thiirans by the reaction of diazoalkanes with thiones has been questioned. It is believed[99] that the interaction of thiobenzophenone with diazomethane leads initially to 1,3,4-thiadiazoline, which is converted into the thiocarbonylide (XXXIV) at –30 °C.

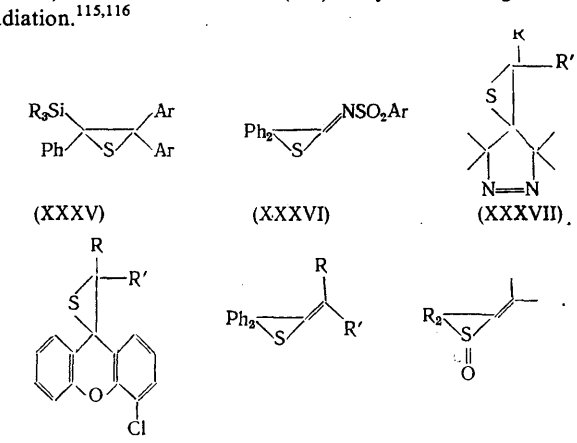


(XXXIV)

The following selective reactions of compound (XXXIV) are believed to constitute confirmation of its formation: isomerisation to 1,1-diphenylthiiran, dimerisation to 2,2,3,3-tetraphenyl-1,4-dithiane, and 1,3-dipolar addition to active dipolarophiles.

The data obtained in the above study[99] apparently reflect the anomalous behaviour of diazomethane in these reactions. Thus the same workers obtained only 3,3-diphenylthioglycidate in the reaction of thiobenzophenone with diazoacetic ester,[100] while the reactions with diazoethane and phenyldiazomethane afforded 3-methyl-2,2-diphenyl- and 2,2,3-triphenyl-thiirans.[101] The formation of thiocarbonylides was not demonstrated in such cases.

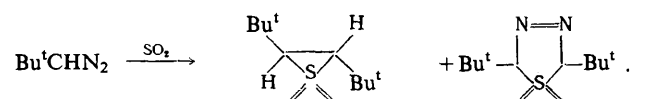
Two examples of this reaction have been investigated.[102–117] Thiirans are formed on interaction of Ph_2CN_2 with tetraphenyl-4-thiopyrone,[102] mono- and di-thio-*N*-arylphthalimides,[103] and *N*-substituted 3-aminoindene-1-thiones.[104] Silylated thiirans (XXXV) have been obtained by the reaction of diaryldiazomethanes with thioacylsilanes,[105,106] while the reactions with sulphonyl isothiocyanates afforded the thiiran imines (XXXVI).[107,108] Diazomethane, diazoethane, diazoacetic ester, and phenyl- and diphenyldiazomethanes interact under mild conditions with tetramethylpyrazoline-4-thione to form the spirothiirans (XXXVII).[109] Diphenyldiazomethane, 4-chloro-9-diazoxanthene, and 9-diazofluorene react with 4-chloroxanthene-9-thione, affording the spirothiirans (XXXVIII).[110] Thiirans have also been obtained in the reactions of 4,4-dimethoxythiobenzophenone with 1-diazo-2,3-dihydroindene,[111] of monothioanthraquinone with 10-diazoanthrone,[112] and of norbornanethiones and thiobenzophenone with diazopropellanes.[113] Diazoketones having the structure $ArCOCHN_2$ react with thiones in a complex manner:[114] aroylthiirans have been obtained only by reaction with fluorene-5-thione. Thioketens and thioketen *S*-oxides react with diazoalkanes to form the corresponding thiadiazolines, which are converted into the thiirans (XXXIX) and thiiran oxides (XL) only on heating or on UV irradiation.[115,116]



(XXXV) (XXXVI) (XXXVII)

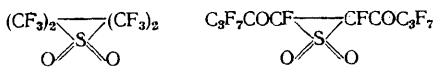
(XXXVIII) (XXXIX) (XL)

The effect of conditions on the mode of reaction of diazoalkanes with sulphur dioxide has been investigated.[117] In the case of t-butyldiazomethane, *trans*-2,3-di(t-butyl)thiiran 1,1-dioxide is formed together with a mixture of *cis*- and *trans*-thiadiazoline 1,1-dioxides whose decomposition affords a mixture of *cis*- and *trans*-thiiran dioxides:



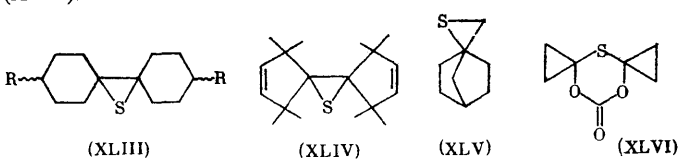
Mixtures of *cis*- and *trans*-thiiran dioxides have been obtained under similar conditions by the reactions of phenyl- and phenylmethyldiazomethanes.

Tetrakis(trifluoromethyl)thiiran 1,1-dioxide (XLI) is one of the products of the reaction of the highly electrophilic hexafluorodimethylsulphonene.[118] The dehydrofluorination of α-fluoro-α-fluoro-sulphonylmethyl perfluoropropyl ketone by the complex $NEt_3.BF_3$ led to 2,3-bis(perfluorobutyryl)-2,3-difluorothiiran 1,1-dioxide (XLII) as a mixture of the *cis*- and *trans*-isomers.[119] Thiiran 1,1-dioxide is believed[120] to be formed as an intermediate in the catalytic high-temperature oxidation of ethylene by sulphur dioxide.

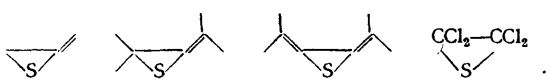


(XLI) (XLII)

Much attention has been devoted to the pyrolytic and photolytic methods of synthesis of thiirans. The thiirans (XLIII)[121,122] and (XLIV)[123] have been obtained by the thermolysis of spirocyclic 1,3,4-thiadiazolines. The relatively unstable methylenethiiran (XLVII) has been synthesised by the vacuum flash pyrolysis of the cyclopropanethione trimer, the episulphide (XLV), or the carbonate (XLVI).[124,125]



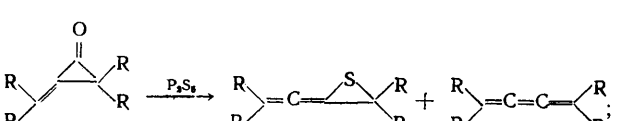
(XLIII) (XLIV) (XLV) (XLVI)



(XLVII) (XLVIII) (XLIX) (L)

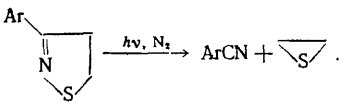
The episulphide derivative of the tetramethylallene (XLVIII) is formed on pyrolysis of the sodium salt of the tosylhydrazone of 2,2,4,4-tetramethylthietanone[126] and on photolysis of tetramethylcyclopropanethione.[127] The vacuum pyrolysis of 2,4-diisopropylidenethietanthione[128] or of the lithium salt of the tosylhydrazone of 4-isopropylidene-2,2-dimethylthietanone[129] has been used to synthesise diisopropylidenethiiran (XLIX). 2,4-Diisopropylidene-1,3-dithietan 1,1-dioxide[130] and tetrachloro-1,3-dithietan 1,1-dioxide[131] are converted on flash pyrolysis into the thiiran (XLIX) and tetrachlorothiiran (L) respectively. The vacuum flash pyrolysis of 2,5-disubstituted 1,3-oxathiolan-5-ones leads to various 1,3-disubstituted thiirans.[132]

The episulphide derivative of buta-1,2,3-trienes were obtained by the thiolation of alkylidenecyclopropanones with phosphorus pentasulphide in pyridine at 80 °C. The episulphide derivatives are partly converted into buta-1,2,3-trienes.[133,134]



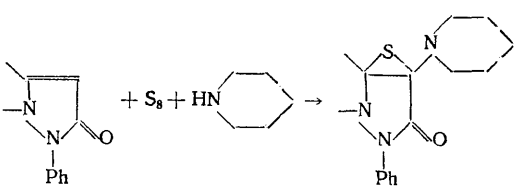
R = Bu^t.

3-Aryl-1,2-thiazolines are converted into thiiran and aryl cyanides on UV irradiation.[135]

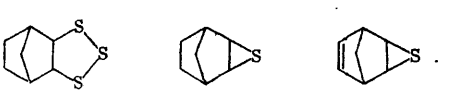


The behaviour of substituted 2*H*-1,3-oxathioles has been investigated under mass spectrometric electron impact conditions.[136] Their cyclodecomposition leads to the thiocarbonylides $RR'C{=}S{-}CBzR''$. Depending on the nature of R and R', the latter cyclise either into thiirans or into the initial oxathioles. The radical-ion reactions of dibenzoyldibromomethane with potassium xanthate[137] and of dibenzoylmethane with sulphur *NN*-bis-(arenesulphonyl)diimide[138] under mild conditions led to tetrabenzoylthiiran, which isomerises to 2,2,4-tribenzoyl-5-phenyl-1,3-oxathiole already during the formation process according to the results of two investigations.[136,139]

Publications have appeared on the syntheses of thiirans from alkenes and elemental sulphur. Irradiation of a mixture of norbornene and S_8 and CS_2 leads to trithiatricyclodecane (LI) and epithionorbornane (LII).[140] Norbornadiene gives rise to the episulphide (LIII) on heating with S_8 in dimethylformamide (DMF) and activation with NH_3.[141] The reaction of antipyrine with sulphur in the presence of cyclic amines leads to an aminothiiran.[142]



The synthesis of natural sesquiterpene episulphide derivatives of caryophyllene, isolated from the essential oil of hops, has been achieved. These compounds are formed on UV irradiation with mixtures of sesquiterpenes with S_8 in cyclohexane or on radiolysis of sesquiterpenes in the presence of phenyl isothiocyanate.[143]



(LI) (LII) (LIII)

New data have also been obtained on the photochemical reaction of COS with ethylene.[144]

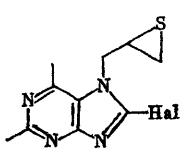
It has been shown that the formation of ethylenethiol is associated with the participation of excited $S(^1D_2)$ atoms. Recommendations concerning the control of the process have been developed.

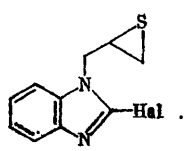
Calculations have been carried out for the $\dot{C}H_2CH_2\dot{S}$ species.[145] Their characteristic feature is the occurrence of the effective spin–orbital interactions of the unpaired electrons, which induces ready $T{-}S$ transitions and ensures the stereospecificity of the formation of the thiiran ring under mild conditions.

4. Reactions of thiirans without ring opening

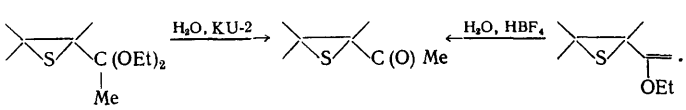
In the presence of alkalies, thioepichlorohydrin reacts in ether with mono-, di-, and tri-halogenoallyl alcohols, dichloropropanol,[28] alkylcellosolves,[29,30] and 3-(triorganosilyl)-substituted allyl[32] and propargyl[33,146] alcohols. Carboxylic acid salts react similarly with thioepichlorohydrin.[147] On treatment with 3-(trimethylsilyl)-propargyl alcohol, the Si—C≡C bond is cleaved and 2,3-epithio-1-propargyloxypropane is formed.[32]

The thiirans (III) have been obtained in the presence of bases under mild conditions from thioepichlorohydrin and alkyl-2-cyanoethylamines.[37] Lithio-*o*-carbaboranes form compounds (VII) in these reactions.[148] Thioepichlorohydrin reacts with sodium, potassium, and ammonium thiocyanates in alcohol to form 2,3-epithio-1-thiocyanatopropane with a small admixture of isothiocyanate, while the reaction with potassium diethyl phosphorothioate affords *OO*-diethyl thioglycidyl phosphorothioate.[149] The epithiopropanes (LIV) and (LV) have been obtained in aprotic media [DMF, dimethyl sulphoxide (DMSO)] by the reaction of thioepichlorohydrin with 8-halogenoxanthines and 2-halogenobenzimidazoles.[150]


(LIV)

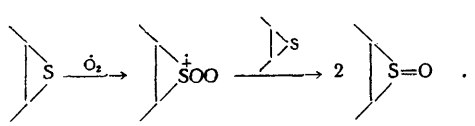

(LV)

The conditions governing the formation of acetylthiiran from acetylthiiran acetal and 2R-2-(α-ethoxyvinyl)thiiran have been investigated.[43]



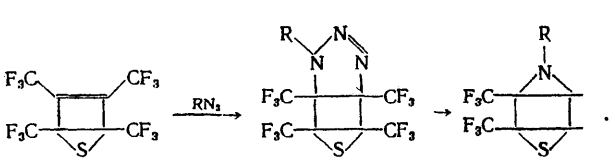
Formylthiiran is formed just as smoothly from its diethylacetal.[42]

The photochemical oxidation of alkylthiirans with oxygen in acetone, CH_3CN, $CHCl_3$, and CH_2Cl_2 leads to thiiran oxides in accordance with the scheme,[151]



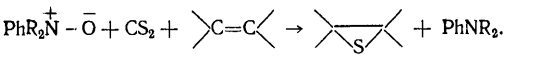
In alcohol, the thiiran ring is opened and the sulphur atom is oxidised. Diallyl-thiirans are indifferent to oxygen on UV irradiation.

The conversion of the stable "Dewar thiophen" into a valence isomer of 1,4-thiazine may serve as an example of the modification of thiirans at the multiple bond of a ring substituent.[152]



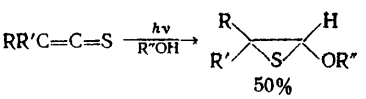
5. Other methods

A novel method of synthesis of thiirans was discovered in a study of the reaction of dimethylaniline oxide with CS_2 in the presence of alkenes.[153]

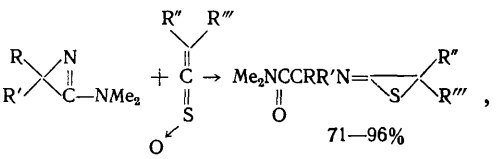


The yield increases with increase in the excess of CS_2 and the alkene. The thiolating agent is believed to be the oxathiiranthione formed from CS_2 and the *N*-oxide.

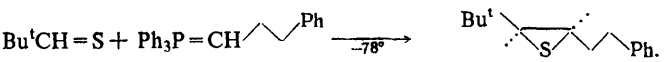
Alkoxythiirans are formed on UV irradiation of thioketens in benzene in the presence of alcohols.[154] The carbene RR'C—CS is believed to be a precursor of alkoxythiirans.



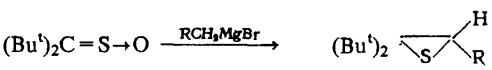
New methods of synthesis of thiiran imines are based on the reaction of dimethylaminoazirines with thioketen *S*-oxides.[155] It is believed that the reaction



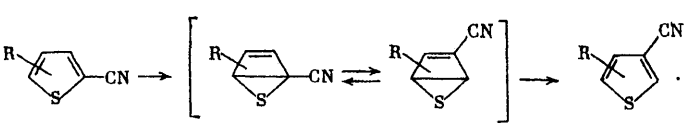
proceeds via a 1,3-dipolar addition mechanism. the formation of an epithio-compound in the reaction of pivaloylthioaldehyde with Wittig reagents has been explained by the formation and reactions of cyclic [2 + 2]adducts.[156]



Thiirans are the main products of the reactions of primary organomagnesium or organolithium compounds with the *S*-oxide of di(t-butyl) thioketone.[157]

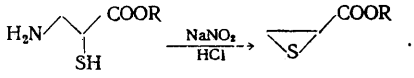


Bicyclic thiirans of the type of "Dewar thiophen" are apparently formed as intermediates in the photolysis of 2-cyanothiophens, which is the cause of their isomerisation to 3-cyanothiophens.[158,159]

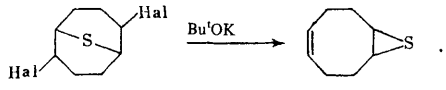


Thiirancarboxylic acids are formed stereoselectively on deamination of aminothiols.[160] The enantiomers of cysteine or its esters afford in this reaction epithioglycidates with the inverted

configuration. The enantiomers of 6-aminopencillanic acid are converted into 3,3-dimethylthioglycidic acid.

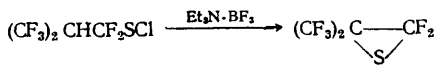


Dihalogeno-derivatives of thiabicyclooctanes and thiabicyclononanes are converted almost quantitatively into monoepithio-derivatives of cyclodienes on dehydrohalogenation by potassium t-butoxide.[161]

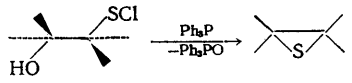


Epithiodiadamantylidene was obtained by the reaction of diadamantylidene with S_2Cl_2 in CH_2Cl_2 at 20 °C.[162–164] In the presence of SCl_2, the epithio-compound is chlorinated to 4-chloro-, 4,4'-dichloro-, and 4,4',8-trichloroepithiodiadamantylidenes.

Epthio-compounds have been obtained[165,166] from sulphenyl chlorides. 2-Hydrooctafluoroisobutanesulphenyl chloride is dehydrochlorinated by the complex $NEt_3.BF_3$ to epithioperfluoroisobutane.[165]



2-Hydroxyalkanesulphenyl chlorides are converted stereospecifically into epithio-compounds on treatment with triphenylphosphine.[167]



The reaction of the monothio-derivative of ethylene glycol with diethoxytriphenylphosphorane in toluene leads to a mixture of thiiran and ethyl 2-hydroxyethyl sulphide.[168]



63% 37%

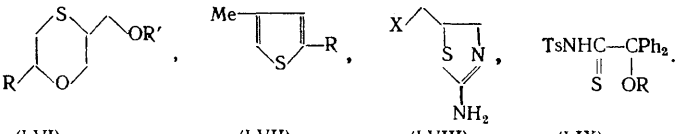
III. Reactivity

Extensive data on the reactivities of a wide variety of thiirans in reactions with hydroxy- and amino-compounds, thiols, CH acids, and various electrophiles as well as data on the behaviour of thiirans in desulphurisation and cyclisation reactions have accumulated during the last decade. There has been considerable expansion of available information about the intramolecular reactions of thiirans with functional group substituents. New quantitative characteristics of the principal types of reactions of thiirans have appeared.

1. Reactions with hydroxy-compounds

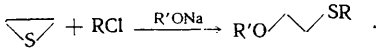
The polymerisation of thiirans in the presence of hydroxy-compounds and basic catalysts prevents the preparative use of this reaction.[1] It had been used earlier only for the synthesis of thietan-3-ol and its derivatives by the opening of the ring of thioepichlorohydrin by certain oxy-anions. This reaction (the thiiran–thietan rearrangement) is being investigated, as before, both for preparative purposes[4–12] and theoretically.[169] At the same time, new examples of the synthetic employment of the nucleophilic opening of the thiiran ring by hydroxy-compounds have appeared.

Thus the interaction of 1-(2-halogenoalkoxy)-2,3-epithiopropanes with alcohols in the presence of bases leads to 1,4-oxathianes (LVI).[29] Propargyl- or propyn-1-yl-thiirans isomerise to thiophens (LVII) on treatment with potassium t-butoxide.[52] Under the conditions of nucleophilic ring opening, *N*-2,3-epithiopropylcyanamide is quantitatively converted into 2-amino-1,3-thiazoline (LVIII).[82] Thiiran imines (XXXVI) react with alcohols under mild conditions to form the amides of α-alkoxy-substituted thiocarboxylic acids (LIX).[107,108] When ethylene sulphide is heated with phenyl acetate in the presence of tri-n-butylamine, 2-phenoxyethyl thioacetate is formed in a high yield.[170]



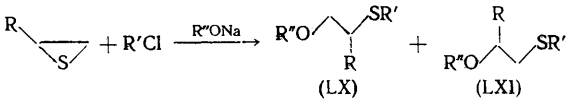
(LVI) (LVII) (LVIII) (LIX)

Another aspect is based on the competing reactions in thiiran–RONa–benzyl chloride systems.[171]



The study of such reactions has shown[172–182] that, in the presence of benzyl and allyl chlorides, monomeric products are formed in 50–80% yield from ethylene sulphide and sodium alkoxides derived from primary aliphatic alcohols, benzyl alcohol, and trifluoroethanol, and also sodium phenoxides. 2-R-Thiirans, including methylthiiran, butylthiiran, phenylthiiran, alkoxy- and aryloxymethylthiirans, and vinylthiiran react similarly in these systems.

It has been established that only alkoxy- and aryloxymethylthiirans interact regioselectively with alkoxy- and aryloxy-anions, mainly in accordance with Krasuskii's rule, i.e. with formation of products having the "normal" structure (LX). The reactions with other 2-R-thiirans afford mixtures of products containing also substances having the "anomalous" structure (LXI).[179–182]



(LX) (LXI)

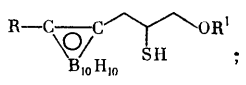
The mixture composition depends significantly on the nature of the oxy-anion and the ring substituent.

The kinetic characteristics and thermodynamic parameters of the reaction permit the conclusion that the reactions proceed via the "push-pull" (Ad_1) mechanism.[173,175–182] The rate-limiting stage in these reactions is the formation of the thiiran–hydroxy-compound ion pair which is facilitated by solvation by proton-donating solvents. The reactivity of this pair is higher than in the analogous reactions of oxirans, which is the reason for the increased tendency of thiirans to be polymerised by hydroxy-compounds. In all the cases investigated, large (in absolute magnitude) negative entropies for the activation of the "normal" opening of the thiiran ring compared with the "anomalous" opening are observed, which is also characteristic of the analogous reactions of oxirans.

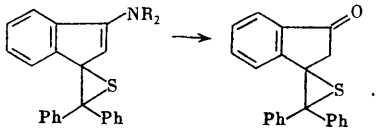
The polymerisation in the reactions of thiirans with hydroxy-compounds can also be suppressed under the conditions of acid catalysis. Thus, in the presence of sulphuric acid, 1,2-epithiodecane interacts with primary aliphatic alcohols to form mixtures of primary and secondary alkoxydecanethiols;[183,184] the isomer ratio depends on the nature of the alcohol and the amount of catalyst. With decrease in the solvating capacity of the solvent, the yield of the monomeric product falls. Tertiary alcohols are ineffective in these reactions in view of their low stability in the presence of acids.

In contrast to epithiodecane, carbaboranylthiirans (VII) react unambiguously with water and alcohols under the conditions of acid catalysis, forming the "normal" structure products (LXII).[71] Under the conditions of nucleophilic catalysis, these reactions lead to oligomers only.[185]

It is noteworthy that the acid-catalysed reactions of thiirans with hydroxy-compounds take place under comparatively severe conditions. Without affecting the thiiran ring, this made it possible to replace the enamine group of compound (LXIII) by the keto-group[104] and to obtain 16,17α-epithiopregnenolene from its acetate.[186] Some of the bicycloalkylidenethiirans are fairly resistant also to bases. This property has been used to remove with the aid of methanol the acetyl protecting group in the diacetates of epithiosecosteroids in the presence of Na_2CO_3.[121]



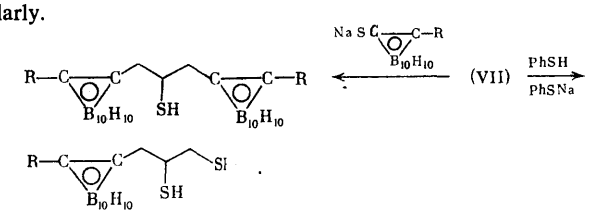
(LXII)



(LXIII)

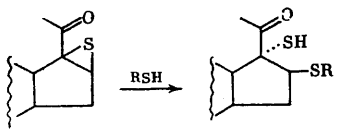
2. Reactions with thiols and thiones

There are few new data on the reactions of thiirans with thiols. The study of the properties of carbaboranylthiirans (VII) established that their interaction with thiophenol in the presence of sodium thiophenoxide in ethanol takes place unambiguously in accordance with Krasuskii's rule.[185] Sodium *o*-carbaboranyl-thiolates react similarly.



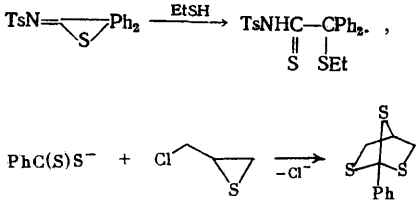
Under the same conditions, carbaboranylthiirans are converted into bismercaptans on reaction with sodium hydrogen sulphide[186] and into trithiocarbabonates on reaction with potassium methyl-xanthate.[72]

Interesting results have been obtained in the study of the reactions of the 16,17α-episulphide ring of 20-ketopregnanes and their hydrazones.[187,188] The reactions of the 3-acetate of 16,17α-epithio-pregnolone with phenylmethanethiol (under the conditions of electrophilic catalysis) or with thioloacetic acid take place stereospecifically in accordance with Krasuskii's rule.

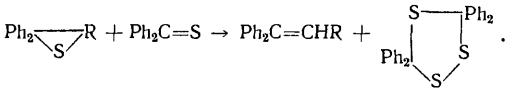


However, ethanethiol splits off sulphur from the epithio-compound under these conditions. The hydrazone of epithiopregnolone undergoes desulphurisation even by thioloacetic acid.

The results of the reactions of thiiran imines with ethanethiol[108] and of thioepichlorohydrin with aluminium dithiobenzoate[189] are of interest.



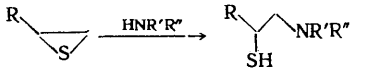
Data have been published on the reactions of thiirans with thiocarbonyl compounds. Di- and tri-substituted thiirans are desulphurised by thiobenzophenones under mild conditions with formation of alkenes and 1,2,4-trithiolans.[190]



Mono- and di-substituted thiolans react with carbon disulphide in solutions in tertiary amines at a high pressure and are converted into trithiocarbonates.[191] 1-(*N*-Carbazolyl)-2,3-epithiopropane readily forms a cyclic adduct with CS_2.[39] In the presence of zinc, cadmium, merury, and ammonium hydrogen sulphides, thiirans react with carbon disulphide and are converted into oligomeric polythio-carbonates.[192]

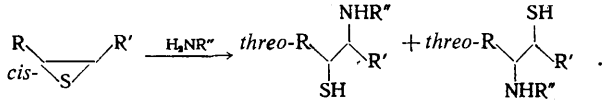
3. Reactions with amines

Reactions with amines constitute the most widely investigated branch of the chemistry of thiirans.[1] In addition to the known quantitative characteristics of the processes involving the opening of the ring in thiirans by amines[1] (Ref. 1, p. 219), a comparative study has been made of the kinetics of the reactions of epoxypropane and epithiopropane with dibutylamine.[193] The results of this study confirmed the qualitative idea that in aprotic media the thiiran ring is opened by dibutylamine more readily than the oxiran ring. The high regioselectivity of the opening of the epithiopropane ring by dibutylamine in conformity with Krasuskii's rule was established. This is a general feature of the reactions of 2-R-thiirans with amines.



The first data on the stereochemistry of this reaction have appeared. It has been shown that *cis*- and *trans*-2,3-dimethyl-thiirans are converted exclusively into *threo*- and *erythro*-aminothiols respectively on heating (90–100 °C) with primary amines (in 200% excess).[194] Mixtures of esters of the regioisomers of anilino-mercaptooctadecanoic acid having the *threo*-configuration have been obtained in the reactions of the methyl esters of *cis*-6,7- and *cis*-9,10-epithiooctadecanoic acids with aniline in the presence of Ag^+ as

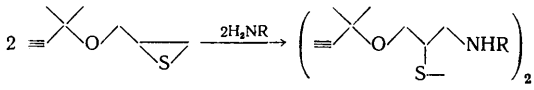
the catalyst; the *trans*-isomers give rise to the analogous products having the *erythro*-structure.[76] Thus the thiiran ring is opened by amines stereospecifically with inversion of the configuration:



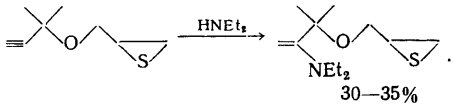
The influence of temperature, solvents, reactant ratio, and the presence of hydroxylated agents on the results of the reaction of 1,2-epithiodecane with secondary amines of different basicity has been investigated in detail.[195] The excess of the amine has a decisive influence on the yield of monomeric products, which indicates the participation of two molecules of the amine in the opening of the ring.

The regioselective formation of aminothiols with the "normal" structure has been established in the reactions of secondary amines with esters based on epithioglycidol. They include 1-triorganylsilylalkoxy(alkenyloxy)-2,3-dimethylthiirans,[32,33] polyhalogenoalkoxymethylthiirans, furfuryloxy- and t-butoxymethyl-thiirans,[31,34] and derivatives of *O*-(2,3-epithiopropyl)hydroxylamine.[196,197]

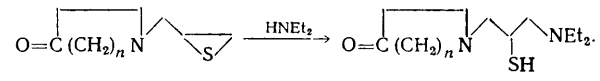
Alkynyloxymethylthiirans react with aliphatic primary amines even in the presence of their excess (100%) only under severe conditions (100–105 °C) with formation of disulphides.[198] Tryptamine, thyramine, and histamine react similarly.[199]



Under more severe conditions (130 °C), the disulphides formed combine with alkylamines via the triple bond. Dialkylamines do not enter into this reaction even in the presence of a large excess of the amine, while in the reaction catalysed by $Et_2O.BF_3$ they add to the triple bond.[200]

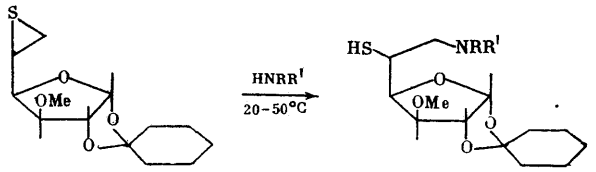


The reactions of *N*-(2,3-epithiopropyl)-substituted 2-pyrrolidinone and 2-piperidinone with diethylamine under severe conditions lead to products with the "normal" structure, which are partly oxidised to disulphides:[38]

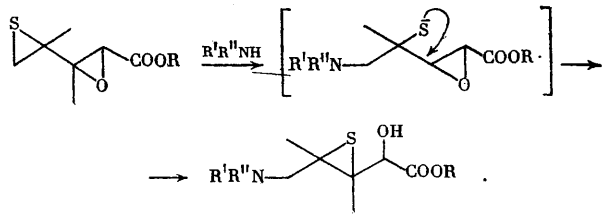


Ring opening via the Krasuskii mechanism has been established in reactions of amines with thiirans having electron-accepting ring substituents—trifluoromethylthiiran[75] and *o*-carbaboranylthiirans.[148,185,187]

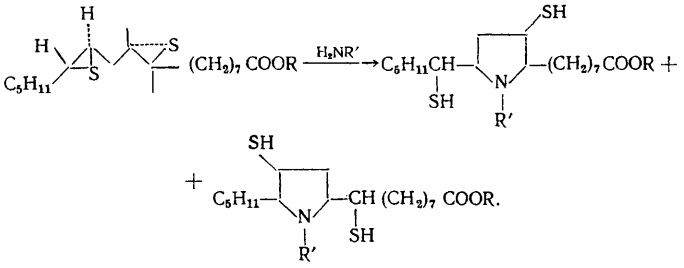
The amination of epithiocarbohydrates by primary and secondary amines and aminoacid esters takes place under unusually mild conditions, which made it possible to obtain aminomercaptoderivatives of glucofuranose,[201] isofuranose,[202] and sorbitol.[203]



The interaction of esters of 2,3-epoxy-4,5-epithiovaleric acids with secondary amines is accompanied by the 2,5-addition of the nucleophile and the 5,3-migration of the thiiran ring, which is a consequence of its "normal" opening and subsequent reaction of the aminothiolate formed.[46]

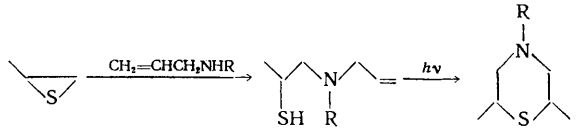


The reactions of primary amines with bisthiirans are accompanied by cyclisation. Thus the only products of the reaction of methyl-, isopropyl-, and benzyl-amines with the *threo*-isomer of *cis*-9,10-*cis*-12,13-diepithiooctadecanoic acid and its esters in aqueous alcohol in the presence of Ag^+ as the catalyst proved to be substituted mercaptopyrrolidines.[204–206]

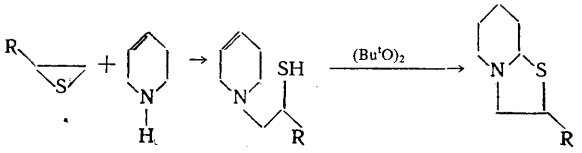


Aniline enters into this reaction with greater difficulty, affording substituted mercaptopyrrolidines with an admixture of aminomercaptothiirans.

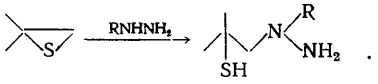
Allyl-, ethylallyl-, and benzylallyl-amines react with thiirans to form mainly the "normal" ring opening products, which cyclise to perhydro-1,4-thiazines on UV irradiation.[207]



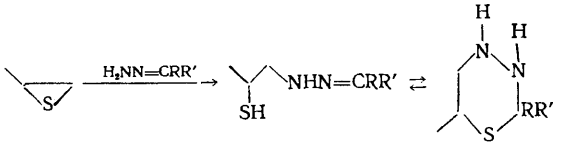
When 2-R-thiirans are heated in benzene with a twofold excess of tetrahydropyridine, secondary aminothiols are obtained in a high yield. They are converted into 7-thia-1-azobicyclo[4.3.0]nonanes under the conditions of a free-radical reaction.[208]



2-Mercaptoalkylation of alkylhydrazines by thiiran, methylthiiran, and epithioisobutane takes place at the substituted nitrogen atom, the ring being opened mainly in accordance with Krasuskii's rule.[209–211]



In benzene at 60 °C, thiiran, methylthiiran, and 2-epithiobutane interact with hydrazones[212,213] to form mainly the "normal" ring opening products, which cyclise reversibly to perhydro-1,3,4-thiadiazines.



The products of the "anomalous" ring opening and the products of the bis-2-mercaptoalkylation of the hydrazones are formed at the same time.

In the search for physiologically active substances, the mono-2-mercaptoethylation of σω-alkylenediamines[13] and the bis-2-mercaptoalkylation of *NN'*-dimethyl-σω-alkylenediamines[214] has been achieved; the products of the reaction of thiirans with *p*-aminophenylacetate esters have been obtained.[14] In the last case, the reaction takes place regioselectively in accordance with Krasuskii's rule.

Under the usual conditions for the 2-mercaptoalkylation of amines, thiiran interacts with macroporous styrene–divinylbenzene copolymers modified by amino-compounds.[215]

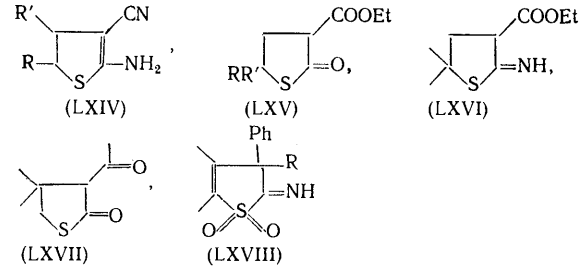
4. Reactions with CH acids

CH acids usually initiate the polymerisation of thiirans under the conditions of nucleophilic catalysis and 3-ethoxycarbonyl-2-imino-tetrahydrothiophens have been obtained earlier only in the reaction with ethyl cyanoacetate (Ref. 1, p. 201). The conditions for the formation of the products of the cyclocondensation of epithio-compounds with other CH acids and their salts have been found recently and the regioselectivity of these reactions has been investigated.

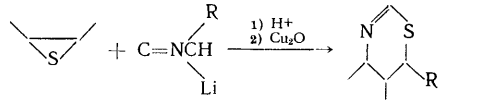
In the presence of NaH in DMSO, malonodinitrile interacts with thiiran, 2-methylthiiran, and 2-phenylthiiran, forming enaminonitriles of the dihydrothiophen series (LXIV) in 50–62% yield. The 2-methylthiiran ring is then opened in accordance with Krasuskii's rule, while that of 2-phenylthiiran is opened contrary to this rule.[216] An enaminonitrile was obtained from thiiran in diglyme in 23% yield,[217] while the product of the cyclocondensation of the enaminonitrile obtained from 2,2-dimethylthiiran in ethanol in the presence of EtONa of the catalyst was obtained in 62% yield.[218]

The reactions of thiirans with malonic ester in alcohol in the presence of EtONa lead to 3-ethoxycarbonyltetrahydrothiophen-2-ones (LXV) in 35–65% yield.[218] 2-Phenylthiiran is converted in the analogous reaction into a mixture of regioisomers (the "anomalous" ring opening product is the main component). 2,2-Dimethylthiiran reacts with cyanoacetic and acetoacetic esters, affording the "normal" ring opening products (LXVI) and (LXVII).[218]

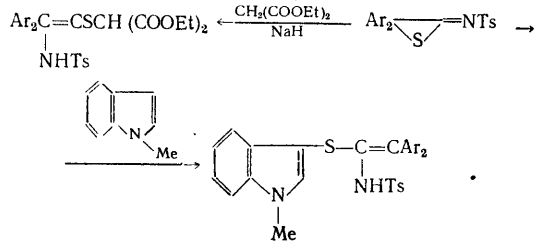
Substituted sodiophenylacetonitriles form the cyclocondensation products (LXVIII) with 2,3-dimethylthiirene 1,1-dioxide in tetrahydrofuran.[219]



The lithio-derivatives of isocyanides add to methylthiiran, epithiocyclohexane, and epithiocyclopentane, affording γ-mercaptoalkyl isocyanides, which cyclise to 4*H*-5,6-dihydro-1,3-thiazines.[220]



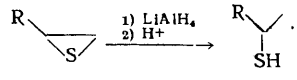
In the presence of NaH, tosyliminothiirans interact with malonic ester,[108] affording enaminosulphides. *N*-Methylindole interacts analogously.



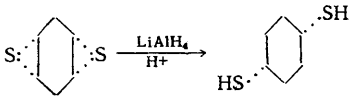
The attempt to involve diisopropylidenethiiran in the reaction with malonic ester in the presence of palladium diacetate as the catalyst was unsuccessful.[128] The product of this reaction was 1,1,4,4-tetramethylbutatriene.

5. Reactions with metal hydrides and organometallic compounds

The latest studies have confirmed the high regioselectivity of the reduction of thiirans by lithium tetrahydroaluminate to secondary thiols. Triorganylsilylalkoxy(alkenyloxy)methylthiirans,[32,33] trifluoromethylthiiran,[75] and also methyl- and phenyl-*o*-carbaboranylepithiopropanes[72] interact with $LiAlH_4$ exclusively in accordance with Krasuskii's rule.

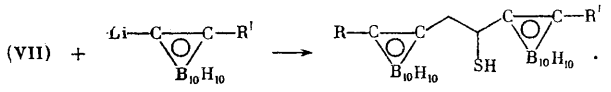


Together with a secondary thiol, an admixture of "anomalous" ring opening product is formed in the reaction of isopropyl-*o*-carbaboranylepithiopropane.[72] The reduction of *cis*-1,2,4,5-diepithiocyclohexane to *cis*-1,4-dimercaptocyclohexane is highly selective.[44]

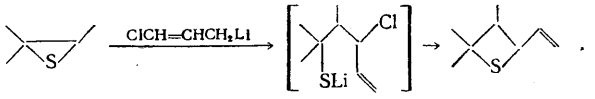


The elimination of sulphur from thiirans has been noted only in isolated instances. For example, the reduction of 4-chlorodiadamantylidenethiiran with $LiAlH_4$ yielded diadamantylidene and not a thiol.[221]

The characteristic features of the reactions of thiirans with organolithium compounds and Grignard reagents have not yet been established. The formation of monomeric products of the reactions of thiirans with organolithium compounds was first demonstrated by Kazantsev et al.[185] and by Ondona et al.[222] Thus carbaboranylthiirans (VII) react with lithio-*o*-carbaboranes to form secondary thiols.[185]

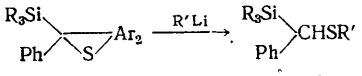


Butyllithium and ethylmagnesium bromide split off a sulphur atom from carbaboranylthiirans.[72,185] At temperatures in the range from −90 °C to −60 °C, substituted thiirans interact with 3-chloroallyllithium to form 2-vinylthietans.[222]

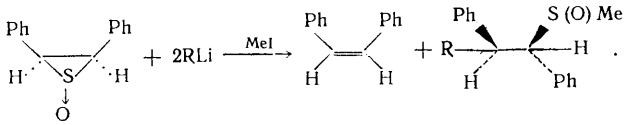


Thioepichlorohydrin is converted in this reaction into the 3-chloro-5,6-epithiohex-1-ene.

The opening of the ring in triorganosilylated triarylthiirans by methyl- and butyl-lithium is accompanied by the cleavage of the C−C bond.[106]

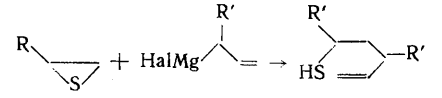


The reactions of butyl- and phenyl-lithium with *cis*- and *trans*-2,3-diphenylthiirans and their *S*-oxides[223] afford the desulphurisation and ring-opening products, which have been isolated as methylated derivatives. *trans*-2,3-Diphenylthiiran and its *S*-oxide are then converted quantitatively into *trans*-stilbene, while the ring opening products with the *threo*-configuration were obtained from the *cis*-isomers together with *cis*-stilbene.



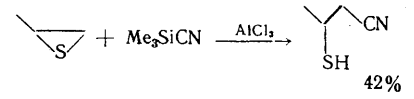
The stereospecificity of the desulphurisation has been explained by the formation and concerted decomposition of intermediate episulphuranes.

New examples of the regioselective interaction of thiirans with Grignard reagents have been described.[224–226] Alkenylmagnesium halides of the allyl type interact with various thiirans to form unsaturated thiols.[224–226]

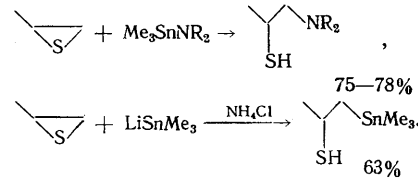


Diisopropylidenethiiran does not react with ethylmagnesium bromide.[129]

The reactions of thiirans with organic derivatives of Group IV elements have been investigated. Trimethylsilyl cyanide interacts with methylthiiran regioselectively in boiling dichloromethane in the presence of $AlCl_3$ as catalyst, affording silylated β-mercaptobutyronitrile together with propene.[227]

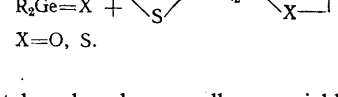


Dialkyl(trimethylstannyl)amides react with methylthiiran and epithiocyclohexane in the absence of the catalyst. In contrast to dialkyl(stannyl)amides, trimethylstannyllithium gives rise to the "normal" ring opening product.[228]

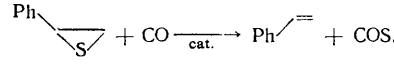


Epthiocyclohexane is partly converted into cyclohexene in this reaction.

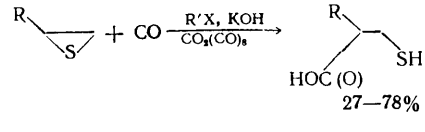
The complex of diethylgermylene and triethylamine interacts with thiiran at 130−150 °C, affording 1,2,5-germadithiolan and ethylene.[229,230] Diethylgermanethione, which undergoes [2 + 3]cycloaddition to thiiran, is believed to be an intermediate in this reaction. This has been confirmed by direct reactions of thiiran with dialkylgermanones and germanethiones.[231]



Metal carbonyls as well as variable valence metal complexes abstract sulphur from thiirans.[232] In the presence of carbon monoxide, rhodium and palladium complexes catalyse the desulphurisation reaction in accordance with the mechanism[233]

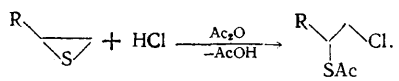


However, the reaction catalysed by $Co_2(CO)_8$ in benzene in the presence of methyl iodide or benzyl bromide and aqueous KOH under phase transfer conditions results in the formation of β-mercaptoalkanecarboxylic acids.[234]



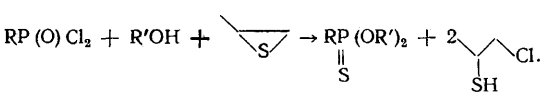
6. Reactions with electrophiles

It has been shown for a large number of examples that the reactions of thiirans with electrophiles are distinguished by a greater variety than had been believed previously. The interaction of carbaboranylthiirans (VII) with concentrated HCl at 0–10 °C resulted in the slow formation (over a period of 10 h) of the "normal" ring opening product. HBr and HI react similarly; in the latter case, the intermediate thiol is oxidised to the disulphide.[71,72,235] In contrast to HCl, HBr interacts with carbaboranylthiirans also in anhydrous media, which can be explained by the specific solvation of the sulphur atom by bromides. HCl in acetic anhydride interacts just as readily with these compounds as with methylthiiran.[70]

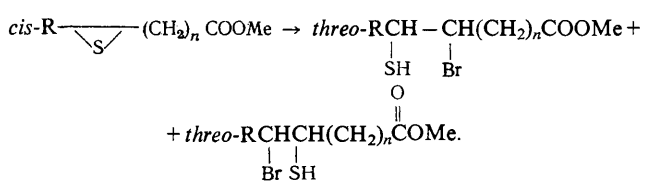


Similar features are characteristic of the reactions of hydrogen halides also with other electron-deficient thiirans, for example, with 3,4-epithiothiolan 1,1-dioxide;[73] in this case too, HCl reacts readily and unambiguously only in acetic anhydride. Under severe conditions, HCl interacts also with trifluoromethylthiiran, affording exclusively the product with the normal structure—a secondary halogenothiol.[75]

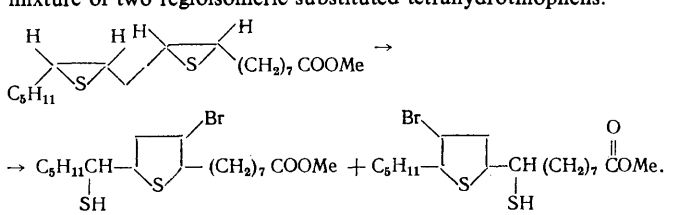
In the absence of electron-accepting substituents in the molecule, thiirans readily combine with HCl in non-polar media. Thus triorganosilylalkoxymethylthiirans[33] and 1-(*N*-phthalimido)-2,3-epithiopropane[236] are converted into secondary halogenothiols in $CHCl_3$ and CCl_4. Aliphatic 2-R-thiirans bind HCl so vigorously that they can be used successfully as hydrogen halide acceptors.[237]



The opening of the ring in thiirans by hydrogen halides is accompanied by the inversion of the configuration. A mixture of *threo*-isomers has been obtained from the esters of higher aliphatic *cis*-epithio-acids on interaction with HBr,[76] while the esters of the *trans*-epithioacids afforded a mixture of *erythro*-isomers.

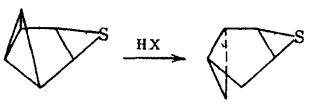


In a number of instances, the interaction of thiirans with hydrogen halides leads to unusual results. The esters of *cis*-9,10-*cis*-12,13-diepithiooctadecanoic acids react with HBr to form a 1:1 mixture of two regioisomeric substituted tetrahydrothiophens.[238]



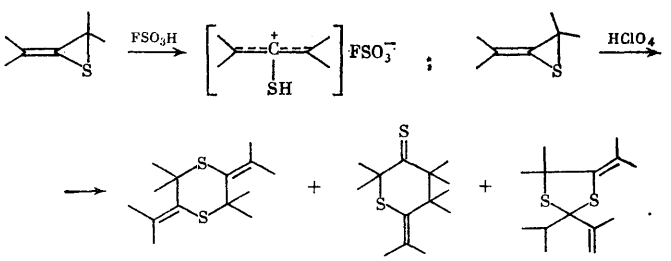
CCl_3COOH reacts similarly.

On treatment with HCl, epithioadamantylidene gives rise to diamantylidene.[221] The reaction of benzvalene sulphide with HCl and acetic acid is accompanied by a skeletal rearrangment.[85]



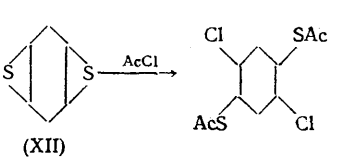
Carbaboranylthiirans (VII) are hydrolysed by 10% H_2SO_4 to mercaptoalkanols in accordance with Krasuskii's rule.[71] The usual thiirans do not polymerise under these conditions.

Tetramethylallene sulphide is protonated by FSO_3H to a stable carbonium ion.[239] However, 70% $HClO_4$ and BF_3 etherate induce its dimerisation.[126,239]



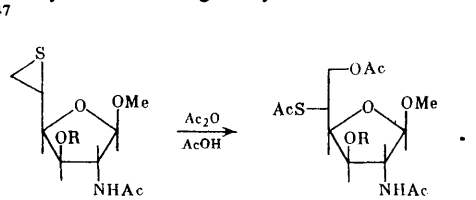
Carbazolylthiiran (VI) is polymerised by dilute inorganic or organic dicarboxylic acids,[240] but acetic acid affords the "normal" ring opening product in 65% yield. Addition in conformity with Krasuskii's rule has been noted also in the reaction of acetic acid with 16,17α-epithiopregnenolones and their hydrazones,[186,188] while the reaction with 1,2-epithiooctane is unambiguous.[241,242]

An uncertain type of ring opening has been observed in the reactions of acetyl chloride with higher 1,2-epithioalkanes[243] and alkylthiomethylthiirans.[244] Carbaboranylthiirans combine with acetyl and benzoyl chlorides in accordance with Krasuskii's rule.[72] Acetyl chloride reacts similarly at 100 °C with trifluoromethylthiiran.[75] The reaction of acetyl chloride with bisepithiocyclohexane (XII) leads to a symmetrical product.[41]

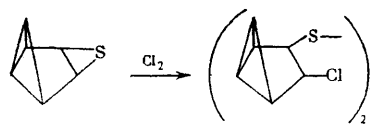


(XII)

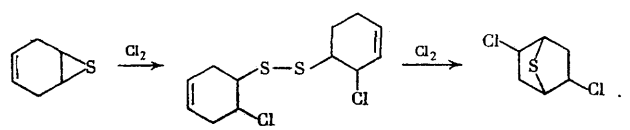
The interaction of higher 1,2-epithioalkanes with carboxylic acid anhydrides in the presence of tertiary amines takes place only under severe conditions and leads to mixtures of 1-acycloxy-2-acylthio-, 2-acyloxy-1-acylthio-, and 1,2-diacylthio-alkanes.[245,246] On the other hand, in acetic acid in the presence of sodium acetate as the catalyst, derivatives of 5,6-epithio-D-glucofuranose interact with acetic anhydride unambiguously in accordance with Krasuskii's rule.[247]



The ambiguity of the ring opening in methylthiiran by chlorine and 2-chloro- or 2-bromo-ethanesulphenyl chlorides (Ref. 1, p. 253) has been confirmed.[248] At the same time, *o*-carbaboranylthiirans (VII) interact unambiguously under mild conditions with chlorine, bromine, iodine,[40,72] and sulphuryl chloride[148] to form the disulphides. The reactions of phthalimidomethylthiiran with bromine[236] and of trifluoromethylthiiran with chlorine[75] are similar. Benzvalene sulphide interacts with chlorine like other thiirans.[86]



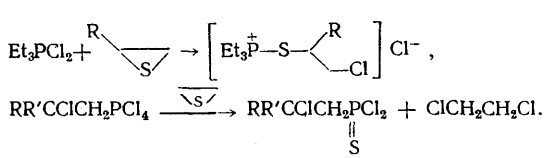
However, the monoepithio-derivatives of cycloalkadienes tend to rearrange under the influence of the halogens and sulphuryl chloride.[249]



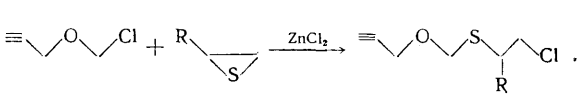
3,3-Ethylenedioxy-4,5-epithiocyclohept-1-ene reacts with halogens to form products corresponding to two possible routes to the opening of the ring.

The reaction of epithiodiamantylidene with SCl_2 leads to the chlorination of the adamantyl groups in the 4-position and then the 4'-position.[162] Methyl iodide abstracts sulphur from these compounds.[211] Refluxing of 4-chloroepithiodiamantylidene with formic acid leads to the substitution of the chlorine atom by the formate group, while the HCl evolved induces the desulphurisation of the epithio-compound formed.[221]

The reactions of 2-R-thiirans with dichlorotriethylphosphorane afforded the relatively stable triethyl-2-chloroalkylthiophosphonium chlorides.[250] Similar products of the reactions of 2-chloroalkyltetrachlorophosphoranes with thiiran decompose readily with evolution of dichloroethane.[251]



The reaction of chloromethyl propargyl ether with 2-R-thiirans in the presence of Friedel–Crafts catalysts results in the preferential formation of products with the "anomalous" structure.[252]

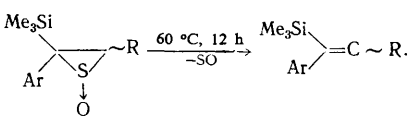


7. Desulphurisation of thiirans

New data refer mainly to the spontaneous or thermal desulphurisation and also to desulphurisation in the presence of metals, organometallic compounds, and trivalent phosphorus compounds.

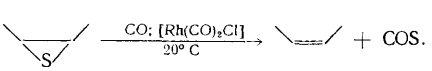
Allene sulphide is converted into allene already at –70 °C,[124,125] while 2,2,3-triphenylthiiran[101] and 2,2-diphenylthiiran[99] split off sulphur after 1 and 15 h respectively at 20 °C. 3-Dialkylaminoindenylidenethiirans (80 °C, 3 h),[104] *cis,trans*-divinylthiirans (90–100 °C),[53] the esters and amides of substituted thioglycidic acids (20–100 °C),[92,93,100,253] the esters of 1,2-epithioethylphosphonic acid,[77] spirothiirans (200–250 °C),[254] and *cis*- and *trans*-dideuteriothiirans (350 °C)[56] are converted into alkenes on heating. Spontaneous or thermal desulphurisation takes place stereospecifically,[53,56,93,253] but in the case of *cis*-2-R-3-R-thiirans it is accompanied by the partial formation of alkenes with the *trans*-configuration.[54]

Several examples of the thermal desulphurisation of thiiran *S*-oxides and *SS*-dioxides have been investigated. For example, the formation of substituted trimethylsilylalkenes from the corresponding *S*-oxides under mild conditions has been demonstrated.[255]



The classical desulphurisation of thiirans by copper bronze at 150–180 °C has been investigated for spirothiirans obtained by the reaction of diazo-compounds with thiopyrans,[102] dithionophthalimide,[103] and xanthones.[110,256] Alkoxythiirans[154] and higher thermal and internal epithioalkanes[257] react under mild conditions (40–90 °C); together with alkenes, alkanes are also formed to some extent under these conditions.

Higher alkenes[257] and secosteroids[121] have been obtained by refluxing the corresponding epithio-compounds with zinc in acetic acid. Thiirans are converted into alkenes on interaction with germylenes,[228] iron pentacarbonyl,[232] and tributyltin hydride in the presence of azobisisobutyronitrile.[257] Stereospecific desulphurisation is catalysed by rhodium complexes in the presence of carbon monoxide.[235]



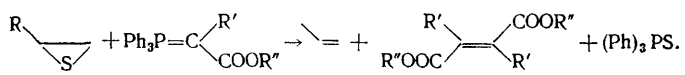
A wide variety of thiirans have been converted stereospecifically into alkenes on refluxing in dimethoxyethane in the presence of lithium.[55] Carbaboranylthiirans[72] and 2-R-3-R-thiirans[156] split off sulphur also on treatment with butyllithium. Butyl- and phenyllithium convert *cis*- and *trans*-2,3-diphenylthiirans or their *S*-oxides into alkenes.[223]

Triphenylphosphine has been used for the desulphurisation of 5-dialkylamino-3,4-epithio-2-hydroxyalkanecarboxylates,[36] a wide variety of 2-R- and 2-R-3-R-thiirans,[90] optically active thiirans,[91] triorganosilylthiirans,[105,106] Dewar's tetrakis(trifluoromethyl)-perhydro-1,4-thiazine,[152] carbaboranylthiirans,[258] and other epithiocompounds. The best desulphurising agents are sometimes PBu_3 and phosphites. Thus, dispirothiirans,[123] tetramethylallene sulphide,[126] and diisopropylidenethiiran[129] are converted into the corresponding alkenes on interaction with PBu_3 and phosphorous tris(dialkylamides). The oxime of 1-acetyl-1-methylthiiran[77] and thiiran imines[155] are readily converted into the oxime of isopropenyl methyl ketone and keten imines respectively on reaction with PBu_3.

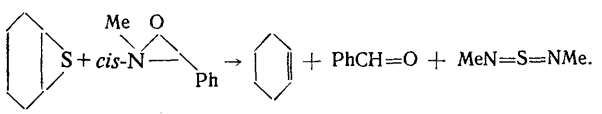
Trialkyl phosphites have been used to synthesise di-, tri-, and tetra-alkylethylenes,[90] *N*-allylpyrimidines,[97] alkylidenepyrazolines,[109] cyclohexylidenecyclohexanes,[122] etc. from thiirans.

New examples of the nucleophilic desulphurisation of thiirans are provided by the conversions into alkenes of triorganosilylated thiirans on reaction with trialkylammonium fluorides[105,106] and by the reactions of carbaboranylthiirans with Grignard reagents.[186] The electrophilic desulphurisation of epithiodiamantylidene has been achieved with methyl iodide.[221] The homolytic elimination of sulphur occurs on the interaction of thiirans with thioketones.[190]

Alkenes are formed from thiiran on reaction of the latter with selenonium ylides (partly)[259] and with phosphonium ylides (quantitatively).[260]

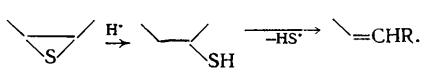


At 20 °C, thiiran, epithiocyclohexane, *cis*- and *trans*-2,3-dimethylthiiran and epithiosteroids are desulphurised quantitatively by oxaziridines.[261]



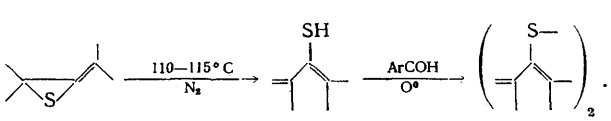
The reaction is stereospecific and is the best method for converting epithio-compounds into alkenes.

cis-2,3-Dimethylthiiran is desulphurised in the gas phase by atomic hydrogen.[262] The quantitative characteristics of such reactions have been obtained for thiiran itself.[263]



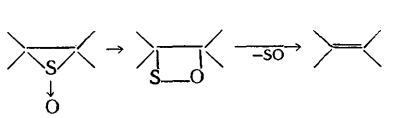
8. Other homolytic reactions

Tetramethylallene sulphide is converted on thermolysis into a 1,3-diene-3-thiol.[264]



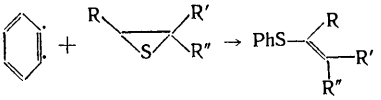
A similar shift of the hydrogen atom takes place also on thermolysis of thiiran with formation of ethylenethiol.[144,265]

The interaction of epithiodiadamantylidene with singlet oxygen leads to desulphurisation and the formation of an *S*-oxide, dioxetan, and an epoxide.[266] 1,2,3-Oxadithiolan-2-thione undergoes similar reactions under the conditions of vacuum thermolysis.[267] It is suggested that *S*-oxides are formed as intermediates.

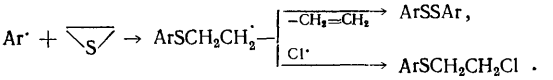


The formation of the *S*-oxide of diisopropylidenethiiran from an epithio-compound and *m*-chloroperbenzoic acid is accompanied by desulphurisation.[128] However, only the *S*-oxide has been obtained from dideuteriothiiran.[56]

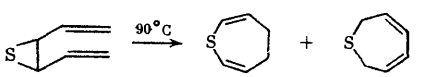
Dehydrobenzene reacts unambiguously with thiirans to form alkenyl phenyl sulphides.[268]



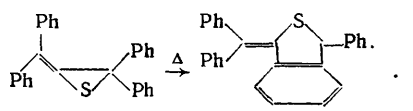
Aryl radicals (produced from ArN_2Cl in the presence of CuCl) react with thiiran to form primary radical species, which are stabilised either by eliminating ethylene or by combining with a chlorine atom.[269]



The homolytic reactions of thiirans are sometimes accompanied by rearrangements. The thermolysis of *cis*-divinylthiiran leads to a mixture of 2,7- and 4,5-dihydrothiepins, while the thermolysis of *trans*-divinylthiiran affords 2,7- and 2,3-dihydrothiepins.[53]



Tetraarylallene sulphides are converted into thiophen derivatives.[115]



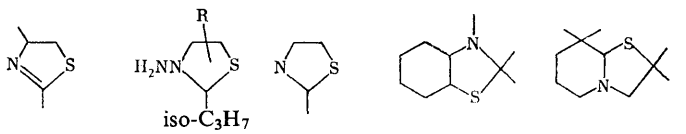
Treatment of α-methylthioglycidamides with amines leads to substituted 1,2,5,6,9,10-hexathiacyclododecanes.[88]

9. Cycloaddition reactions

The earlier ideas concerning the cycloaddition of thiirans to nitriles in the presence of strong acids were tested in 1978 on a large number of examples.[270] The high regioselectivity of these reactions, leading to thiazolines with the "normal" structure (LXIX), was demonstrated. The [2 + 3]cycloaddition of thiirans to the C=N bond in aldehyde hydrazones was described for the first time by Shevchenko and Potekhin.[212] Isobutyraldehyde hydrazone reacts with thiiran, methylthiiran, and 2,2-dimethylthiiran to form 3-amino-thiazolidines;[213] asymmetric thiirans afford a 1:1 mixture of regioisomers of compound (LXX).

The unusually easy (20°, 5 h) cycloaddition of thiiran to the C=N bond in alkaloids belonging to the C_{20} diterpenoid series has been described;[271] in the presence of an excess of the thiiran, cyclic adducts are formed almost quantitatively. The cycloaddition of thiirans to azomethines has been studied systematically,[207,272–274] the *N*-alkyl- and *N*-aryl-imines of aromatic aldehydes and acetone, pyrrolines, tetrahydropyridines, and dihydroquinolines have been made to react with thiiran, methylthiiran, 2,2-dimethylthiiran, and epithiocyclohexane. The ring opening in conformity with Krasuskii's rule results in the formation of a mixture of (*Z*)- and (*E*)-isomers of thiazolidines of the type (LXXI), (LXXII), and

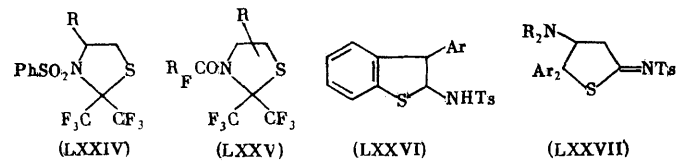
(LXXIII). The diethylacetal of formylthiiran reacts similarly with Schiff bases.[275]



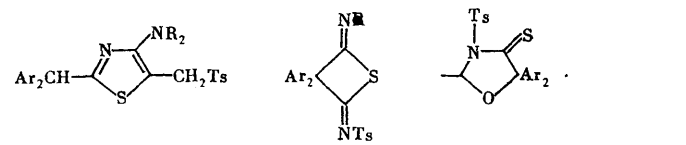
(LXIX) (LXX) (LXXI) (LXXII) (LXXIII)

The highly electrophilic hexafluoroacetone benzenesulphonylimine reacts with thiirans to form the cyclic adducts (LXXIV) only after the preliminary formation of $n\pi$-complexes (–60 °C).[276] The more electrophilic hexafluoroacetone polyfluoroacylimines vigorously open the ring in thiiran and methylthiiran even at –78 °C, which leads to a mixture of the regioisomers of compound (LXXV).[277]

The iminothiirans (XXXVI), obtained from diaryldiazoalkanes and arenesulphonyl isothiocyanates, enter vigorously into the cycloaddition reaction.[107,108,278,279] By virtue of their ready conversion into the acyclic dipolar state, they are converted into 2,3-dihydrobenzothiophens (LXXVI) even in boiling chloroform. At 0 °C, they react with enamines to form 2-iminoperhydrothiophens (LXXVII), with ynamines to form thiazoles (LXXVIII), and with isonitriles to form diiminothietans (LXXIX). They react with aldehydes at 20 °C to form oxazolidinethiones (LXXX). The reactions are highly regiospecific and stereospecific.



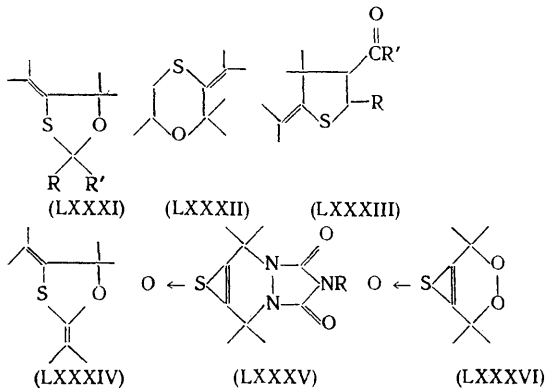
(LXXIV) (LXXV) (LXXVI) (LXXVII)



(LXXVIII) (LXXIX) (LXXX)

New types of cycloaddition reactions have been discovered in the study of the reactions of allene sulphides with carbonyl compounds and oxirans.[280,281] Tetramethylallene sulphide interacts with aldehydes and ketones on heating (110–115 °C) or in the presence of an electrophilic catalyst with formation of 1,3-oxathiolans (LXXXI). The analogous reaction with oxirans leads to the cyclic [3 + 3]adduct (LXXXII), while the reaction with αβ-unsaturated ketones affords acylthiophanes (LXXXIII). Diphenylketen gives rise to the oxathiolan (LXXXIV).

The *S*-oxide of diisopropylidenethiiran enters into Diels–Alder reactions with electron-accepting dienophiles at 20 °C. Thus the *S*-oxide reacts with 1,2,4-triazolidinediones to form the cyclic [4 + 2]adduct (LXXXV).[282] Photochemical oxidation with oxygen in the presence of tetraphenylporphyrin also leads to the cyclic [4 + 2]adduct (LXXXVI). The latter proved to be an active dienophile which readily enters into cycloaddition reactions with cyclodienes.[283]



(LXXXI) (LXXXII) (LXXXIII)

(LXXXIV) (LXXXV) (LXXXVI)

Intramolecular cyclisations are characteristic of thermal reactions of a wide variety of tetraallene sulphides[115] and divinylthiirans.[53] The high-temperature reactions of the latter usually lead to mixtures of 4,5-dihydrothiepins, 2-vinylthiophen, and desulphurisation products. 3-Phenyl-2-vinylthiiran is converted under these conditions into a mixture of 2-phenylthiophen and 2-phenyl-2,3-dihydrothiophen.[284]

The formation of cyclic [3 + 2]adducts has been noted in the homolytic opening of the thiiran ring in the presence of aromatic compounds. For example, benzothiophen has been obtained by the thermolysis of thiiran in chlorobenzene.[285]

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The synthesis and properties of *N*-(2,3-epoxypropyl)carbazoles and the oligomers based on them

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ABSTRACT. The principal methods of synthesis of *N*-(2,3-epoxypropyl)carbazoles and the oligomers based on them, their physicochemical optical, photophysical, and electrical properties, as well as the practical applications of carbazole-containing polymers are examined.

The bibliography includes 177 references.

Contents

I. Introduction 425
II. Methods of synthesis and properties of *N*-(2,3-epoxypropyl)carbazoles 425
III. Some characteristic features of the synthesis of *N*-(2,3-epoxypropyl)carbazole oligomers 426
IV. Properties of *N*-(2,3-epoxypropyl)carbazole oligomers 428

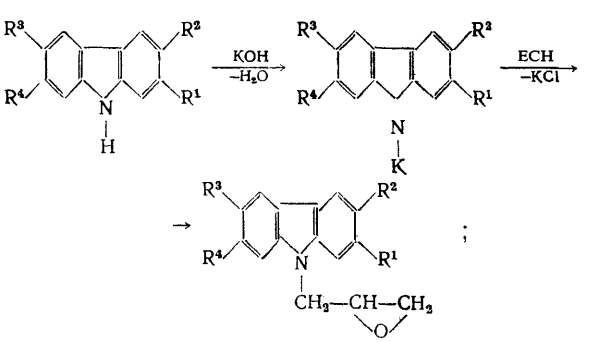
I. Introduction

In connection with the development of technical means for the recording, storage, and reproduction of information, there has been recently an appreciable growth of demand for new non-silver photographic processes, among which electrophotographic processes occupy a notable place. One of the thermoplastic materials with fairly high chemical, radiation, and thermal stabilities as well as effective electrically insulating properties and most widely used in electrophotography is poly-*N*-vinylcarbazole (PVCA).[1] The electrophotographic materials based on PVCA are light, can be readily charged (positively and negatively), are fairly transparent, and have an effective resolving power. On the other hand, the high softening temperature, low adhesion to different substrates, and poor film-forming properties characteristic of PVCA hinder its wide-scale employment in electrophotography. Since the photoelectric properties of PVCA are determined primarily by the presence and relative disposition of carbazole groups, presumably, on passing from carbochain polymers to polyethers containing analogous substituents with extensive systems of conjugated bonds, the photoelectric properties of the system will not change significantly. As a result of the appearance of ether linkages in the main chain of carbazole-containing polymers, one should then expect a decrease in the softening temperature and an improvement in the adhesion and film-forming properties. One of the cheapest and most promising types of photosemiconducting polyethers used as thermoplastic materials in electrophotography are poly-*N*-epoxypropyl carbazoles (PEPC), obtained by the polymerisation and copolymerisation of *N*-(2,3-epoxypropyl)carbazole (EPC) and its derivatives.

Although little more than 10 years have elapsed since the appearance of the first communications on the synthesis of EPC derivatives and oligomers based on them, fairly extensive information has accumulated in the literature on the synthesis, structures, and the physicochemical and photophysical properties of such materials. These results have been reflected in one way or another in a series of reviews devoted to questions of the synthesis and properties of carbazole-containing polymers.[1–4] In writing the present review, the authors endeavoured as far as possible to arrange systematically and analyse the available information (including patent data) on the synthesis and properties of monomeric and oligomeric EPC published after 1973.

II. Methods of synthesis and properties of *N*-(2,3-epoxypropyl)carbazoles

Epoxypropylcarbazoles are obtained by treating the corresponding *N*-metallated carbazole with epichlorohydrin (ECH) in accordance with the following scheme:



R^1—R^4 = H, Br; R^1 R^4 = H; R^2, R^3=Cl; R^1, R^2, R^4=H, R^3=NO_2.

The reaction is carried out in benzene,[5] ethyl methyl ketone,[6] a mixture of xylene isomers,[8] or dimethylformamide.[9–11] According to Sazonenko et al.[9] and Inaki et al.,[10] the potassiocarbazole formed initially reacts subsequently with epichlorohydrin to form EPC. Since potassiocarbazole is readily hydrolysed in the presence of water, the water evolved in the interaction of carbazole with potassium hydroxide retards the formation of potassiocarbazole and hence EPC.

EPC is also obtained by fusing carbazole together with KOH at 200–250 °C with subsequent treatment of *N*-potassiocarbazole with epichlorohydrin in benzene.[5] The interaction of carbazole and its derivatives with epichlorohydrin in the presence of alkalis has been studied by Rovkina.[7] It has been shown that the interaction of carbazoles with epichlorohydrin can be achieved under mild conditions and in one stage in dipolar aprotic solvents in the presence of solid alkalis. The formation of two types of substances was observed under the conditions investigated—*N*-(2,3-epoxypropyl)carbazoles and dicarbazolylpropanols, the process comprising consecutive stages with respect to epichlorohydrin and parallel stages with respect to carbazole. The selectivity of the conversion of carbazole into the products indicated is mainly influenced by the carbazole: epichlorohydrin ratio.

The low yield of the target product (up to 24%), the long reaction time,[8] the formation of 1,3-di(*N*-carbazolyl)-2-propanol as a side product, and the consumption of large amounts of solvents in the purification of EPC[6] are significant disadvantages of the above methods of synthesis of EPC.

Much better results have been obtained in the reaction of carbazole with sodium ethoxide and epichlorohydrin in purified dimethylformamide (DMF)[11] and also in the presence of substances forming hydrates such as alkali metal carbonates and sulphates.[12] Under these conditions (30–40 °C, 20–30 min), the target product is obtained in 99% yield.

Table 1. Characteristics of epoxypropylcarbazoles.

Monomer	M.p., °C	Method of preparation
EPC*	111–112	[8]
	108–109	[5, 9]
	108	[6]
	110–111	[10, 11]
	112–113	[12]
BEPC**	54–56	[14]
DBEPC*	149–150	[13]
	145–147	[14]
TBEPC**	154–156	[14]
CEPC*	72–73	[11]
DCEPC*	143–144	[11]
NEPC**	146–148	[13]
GBC**	107	[15]

* White crystals. ** Yellow crystals.

Epoxy-derivatives of carbazole have been obtained by the reaction of substituted carbazoles with epichlorohydrin in the presence of KOH: 3-chloro- and 3,6-dichloro-EPC (CEPC and DCEPC), 3-nitro-, 3-bromo-, and 3,6-dibromo-EPC (NEPC, BEPC, and DBEPC), 3,6,8-tribromo-EPC (TBEPC), and 1,3,6,8-tetrabromo-EPC derivatives (data in Table 1). *N*-Glycidyl-7*H*-benzo[*c*]carbazole (GBC), capable of giving rise to polymers and copolymers with a higher diffraction efficiency, was obtained by treating the lithio-derivatives of 7*H*-benzo[*c*]carbazole with epichlorohydrin.[15]

Epoxypropylcarbazole and its derivatives are crystalline substances soluble in tetrahydrofuran, DMF, acetone, dimethyl sulphoxide, aromatic hydrocarbons, and chloroform. All the monomers are insoluble in alkanes and are sparingly soluble in ether and alcohols.

After the isolation of the epoxy-derivatives of carbazole from the reaction mass, they were purified by both recrystallisation[5–15] and by sublimation. The optimum conditions for the sublimation of EPC have been published.[13] Under the selected optimum conditions, an EPC with a high degree of purification and m.p. 113 °C was obtained.

Qualitative[6,11,16] and quantitative[17,18] methods for monitoring the reactions of carbazole and its derivatives with epichlorohydrin by thin-layer chromatography (TLC) have been developed.

The IR absorption bands of EPC derivatives have been assigned.[19] The UV absorption maxima of substituted EPC undergo a bathochromic shift relative to EPC and to a greater extent the more polar the substituent in the carbazole nucleus.[14,20]

Measurements have been made of the photocurrents and dark currents in EPC.[20] The dark currents I_d for EPC, DBEPC, and NEPC are respectively 1.5×10^{-12} A (at 3 V), 1.2×10^{-13} A (at 14 V), and 5.5×10^{-11} A (at 7 V). The ratios of the photocurrent to the dark current (I_{ph}/I_d) at 4 V and for a light energy $W = 6.8 \times 10^{-3}$ W cm^{-2} are respectively ~5, 10, and 20 for EPC, DBEPC, and NEPC.

III. Certain characteristic features of the synthesis of *N*-(2,3-epoxypropyl)carbazole oligomers

The most important properties of epoxypropylcarbazoles are their ability to polymerise on treatment with catalysts with opening of the epoxide ring and the formation of linear oligoethers. Methods are known for the synthesis of oligomers and cooligomers of epoxypropylcarbazoles by their polymerisation in the presence of anionic, cationic, and coordination catalysts and also by the chemical modification of oligomers and by polymer-analogue transformations.

1. Anionic polymerisation

EPC are known to polymerise on treatment with anionic catalysts such as potassium hydroxide,[10,21–23] sodium phenoxide,[24,25] dimethylbenzylamine,[26] triethylamine and water,[7,27] sodium *p*-nitrophenoxide,[28] and the radical-ion salt of sodium and naphthalene (SN),[29,30] zinc acetate and aluminium isopropoxide,[31] and potassium t-butoxide.[32]

The study of the polymerisation of EPC in both homogeneous and heterogeneous media has shown that the polymerisation takes place most effectively in a heterogeneous medium,[21,23,26] especially in bulk on treatment with KOH. The polymerisation of EPC in bulk on treatment with KOH depends to a large extent on the state of the catalyst surface.[21–23] The rate of polymerisation and hence the yield of the polymers are higher when the polymerisation is carried out using finely dispersed KOH.[33]

The kinetic curves for the heterogeneous polymerisation of EPC in bulk on treatment with KOH[21,23,33] indicate the absence of an induction period in contrast to polymerisation on treatment with SN[30] and sodium *p*-nitrophenoxide.[28] The rate of polymerisation which increases with increase in temperature and catalyst concentration is independent of the initial stage and monomer concentration, subsequently diminishes for high degrees of conversion.

The rate of polymerisation of EPC at 120 and 140 °C and for catalyst concentrations ranging from 1 to 8 mol% are 1.38×10^{-4} and 4.84×10^{-3} s^{-1} [21] and 1.0×10^{-3} and 2.0×10^{-3} s^{-1}.[33]

As on initiation by treatment with SN,[30] the introduction of a fresh portion of the monomer after its quantitative conversion in the first stage leads to a non-linear increase in the degree of polymerisation as a function of the degree of conversion of the monomer and to a slight broadening of the molecular weight distribution. Thus, after the formation of the EPC polymer (140 °C, yield 92%) with a number-average molecular weight $\overline{M}_n$ = 1100,[33] the repeated introduction of the monomer results in the formation of a product with $\overline{M}_n$ = 1560 in 90% yield. A similar picture has been observed in studies[21] where $\overline{M}_n$ for the polymer formed in the first and second stages was 1560 and 2300 respectively.

The study of the polymerisation of EPC in a homogeneous medium[24,28–32] and in particular in DMSO in the presence of potassium t-butoxide[32] indicates a high initial rate of the process and its subsequent diminution. According to the authors, the main cause of this is the large difference between the rates of initiation and chain propagation as a consequence of the appreciable nucleophilicity of the t-butoxide ion compared with the nucleophilicity of the active centre. The PEPC obtained on treatment with the above catalysts contains in its structure hydroxy- and propenyl end groups as well as a small number of allyl end groups, formed as a result of the partial isomerisation of the propenyl end groups.[34] It has been shown that hydrolysis of the unsaturated propenyl ether end groups by concentrated hydrochloric acid results in the formation of hydroxy-groups.

On the other hand, the low molecular weights of the EPC polymerisation products obtained in the presence of KOH and other anionic catalysts, the absence of a linear increase in $\overline{M}_n$ with the degree of the conversion of the monomer, the non-proportional increase in the molecular weight after the addition of a fresh portion of the monomer, the presence of unsaturated end groups in PEPC, and also the difference between the calculated and experimental molecular weights indicate chain transfer in the polymerisation process. It has been suggested that chain propagation is stopped by chain transfer to the monomer[21–23,30–33] and, in the case of polymerisation of EPC in dimethyl sulphoxide (DMSO) on treatment with alkali metal alkoxides, also as a result of chain transfer to the solvent.

However, in the polymerisation of EPC on treatment with alkali metal phenoxide in an aprotic solvent (dioxane) in the presence of dibenzo-18-crown-6, it has been possible to reduce the factor associated with chain transfer to the monomer and to obtain PEPC with $\overline{M}_n$ = 4300.[24]

Among the EPC derivatives, poly-3,6-dibromo- and poly-3-nitro-EPC (PDBEPC and PNEPC)[33] and poly-3-chloro-, poly-3-methyl-, and poly-3-acetyl-EPC[34] have been obtained by the anionic mechanism. In the polymerisation of DBEPC in the presence of KOH, the reaction order with respect to the catalyst is 2/3 with a polymerisation process activation energy of 79 kJ mol^{-1}.[33]

2. Cationic polymerisation

N-(2,3-Epoxypropyl)carbazole and its derivatives polymerise[9,35,41] and copolymerise[37,42,43] fairly vigorously in the presence of cationic catalysts. The increased reactivity of EPC derivatives in polymerisation reactions on treatment with boron trifluoride etherate[35,37–40] and tin tetrachloride[36,38] can be accounted for by the electro-donating contribution of the substituent, which promotes an enhancement of the electron density on the epoxy-group.

A characteristic feature of the cationic polymerisation of EPC is the high rate of reaction in the initial stage and the rapid attainment of the limiting degree of conversion of the monomer, which increases with increase in the catalyst concentration. It has been established that, in the polymerisation of EPC in the presence of $BF_3.OEt_2$, the reaction orders with respect to the monomer and the initiator are 1.0 and 0.9 respectively, while the polymerisation rate constant is described by the equation:

$$K = 6.7 \cdot 10^2 \exp\left(-\frac{3.73 \cdot 10^3}{RT}\right). \quad (1)$$

The molecular weight of the oligomers in the cationic polymerisation does not exceed 2000 and depends little on the catalyst concentration. The limitation of the molecular weight in the polymerisation process is caused by the high contribution of the chain transfer reaction and by the deactivation of the active centres.[37] In the polymerisation of EPC in the presence of $SnCl_4$ in dichloroethane, the initial rate of reaction is directly proportional to the monomer and initiator concentrations and the molecular weight of PEPC increases on reducing the temperature and with increase in the initial monomer concentration.[38]

The higher glass point of the EPC oligomers obtained in the presence of $BF_3.OEt_2$ compared with the oligomers synthesised in the presence of KOH can be explained by the presence of macrorings in the PEPC structure.[39]

3. Other methods of synthesis of the oligomers

EPC oligomers and cooligomers have been obtained on treatment with $ZnEt_2$ and $AlBu^n_3$ [35] and also by means of polymer-analogue transformations[44–46] and by the chemical modification of the PEPC structure.[27,47–49] A high-molecular-weight PEPC has been synthesised[44] with a high degree of conversion by the reaction of the potassium or sodium salt of carbazole with polyepichlorohydrin.

The interaction of the terminal OH groups of PEPC with bi-functional reagents such as dichloromethylphenylsilane and 2,4-tolylene diisocyanate[45] leads to carbazole-containing block copolymers exhibiting a high photosensitivity and diffraction efficiency.[45] Block copolymers of EPC with epichlorohydrin and glycidyl dihydroabietate have been obtained by the reaction involving chain transfer to the polymer with dissociation. In each case, the polymerisation of one of the monomers was carried out in the presence of the other oligomer.[46] However, the analogous statistical cooligomer of glycidylcarbazole (GC) with epichlorohydrin exhibits a higher photosensitivity as a result of the formation of a more effective charge transfer complex (CTC) in this case. The statistical block copolymers of EPC with NEPC (in the presence of KOH as the catalyst) have been described.[13] The chemical modification of PEPC[43,47–49] and of its brominated derivatives[48] constitutes a route to materials with electrophotographic sensitivity over a wide spectral range, which are promising for use in electrophotography. The formyl derivative of PEPC has been condensed[47] with 2,4,5,7-tetranitrofluorene and 6-methyl-2,4-diphenylpyrylium at 30 – 100 °C.

The oligomers obtained were compatible with PVCA and PEPC in any proportions, affording uniform films with a photosensitivity up to 650 nm.

The molecular weights of the cooligomers based on EPC and its di- and tri-bromo-derivatives with butyl glycidyl ether (BGE) are close to those of the EPC homopolymers, while the molecular

weights of the cooligomers of EPC with allyl glycidyl ether are significantly higher. The cooligomer films exhibit two physico-mechanical and optical properties and more effective adhesion to various substrates.[43,48] The integral photosensitivity of the EPC cooligomers increases linearly with increasing fraction of the comonomer.[48] Thus the cooligomer of DBEPC with BGE, sensitised by 9-dicyanomethylene-2,4,7-trinitrofluorene (DCMTNF) has a sensitivity higher by a factor of 4–5 in the range 600–700 nm than that of the unmodified PDBEPC.[43,48] Bromo-substituted PEPC, which have been tested under holographic recording conditions (λ = 633 nm) on layers 1.0–1.5 μm thick with sensitisation by trinitrofluorene, have a diffraction efficiency up to 20%.[48]

4. Some characteristics of the polymerisation of epoxypropylcarbazoles

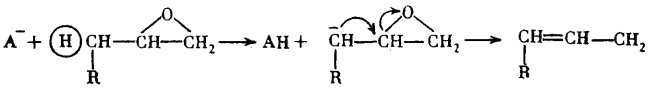
The study of the anionic polymerisation of EPC and its derivatives has shown that SN is a less effective initiator[30] than other catalysts of polymerisation in a homogeneous medium.[24,28,29,31,32]

The nitro-derivatives of EPC do not polymerise on treatment with SN, which is associated with the ease of electron transfer from SN to the nitro-group of the monomer; this has been confirmed by the results of a polarographic study: the half-wave potentials $E_{1/2}$ for NEPC and naphthalene are respectively −1.28 and −2.53 V. DBEPC partially polymerises in the presence of SN with elimination of sodium bromide. The elimination of bromine is also promoted by electron transfer from the SN molecule to DBEPC with the apparent subsequent formation of the DBEPC carbon ion.[50] The partial elimination of bromine with formation of KBr has also been observed in the polymerisation of DBEPC on treatment with solid potassium hydroxide at high temperatures.[33]

The induction period in the polymerisation of EPC in the presence of SN is apparently associated with the formation of low-molecular-weight polymeric alkoxides and with their insolubility in THF and also with the possibility of electron transfer from SN to the carbazole nucleus. The induction period depends on the initiator concentration and the polymerisation temperature, diminishing as the latter increase.[30]

Since gel-permeation chromatographic data rule out the degradation of the polymer chain, the low molecular weights and the absence of a linear relation between $\overline{M}_n$ and the degree of conversion are evidence for chain transfer to the monomer, which is so significant for substituted epoxides.[51]

According to Akhmedov et al.,[30] unsaturated terminal groups are formed as a result of chain transfer to the monomer via the proton β-elimination mechanism:[52]



R = N-carbazolyl.

The study of the polymerisation of EPC in the presence of SN in solution in THF at catalytic complex concentrations in the range 6.1×10^{-3}–1.2×10^{-1} M suggests that the polymerisation proceeds via a stepwise anionic mechanism. Initiation at high initial initiator concentrations is effected by dianions, while at lower concentrations it is initiated by comparable amounts of the mono- and di-anions. The polymerisation is of the living centres type,[53] i.e. in the presence of material chain termination reactions but with propagation of kinetic chains.

The rate of polymerisation of EPC on treatment with KOH should be described by the following equations in the initial polymerisation stage:[13]

$$W = \frac{d[M]}{dt} = k_1 \cdot [M]_0^0, \quad (2)$$

$$W = k_2 [KOH]^n, \quad (3)$$

where W is the rate of polymerisation in the initial stage, [M] the monomer concentration at time t, $[M]_0$ the initial monomer concentration, t the polymerisation time, k_1 and k_2 are polymerisation rate constants, [KOH] is the catalyst concentration, and n the reaction order.

The experimental data indicate a satisfactory fulfillment of the law $W \propto [KOH]^{2/3}$ in the initial stage, which agrees with the occurrence of the reaction on the interface.[13]

The zero reaction order in the initial stage of the polymerisation with respect to the monomer is evidently associated with the fact that the fraction of the catalyst surface covered by the monomer is close to unity and the rate therefore ceases to depend on the monomer concentration.

The decrease in the rate of polymerisation after the attainment of a definite degree of conversion of the monomer, which is particularly abrupt at low initial catalyst concentrations, is associated with the accumulation in the system of an inactive oligomer, which prevents the access of the monomer to the catalyst surface. This is confirmed by the fact, when the EPC polymerisation is carried out in the presence of an EPC oligomer obtained in an independent experiment, the degree of conversion of the monomer in the initial stage diminishes sharply. When the catalyst is kept beforehand in contact with oligomers obtained in an independent experiment, the polymerisation of the monomer introduced subsequently is inhibited, which indicates the "coating" of the catalyst by the polymerisation products.[33] The above features are somewhat different from those in the polymerisation of EPC in the presence of KOH with vigorous stirring.[21]

The occurrence of the preferential chain transfer to the monomer and not to another reactant with a mobile hydrogen atom (for example, water when aqueous alkali is used as the catalyst, or the polymer) is confirmed by the fact that, in the polymerisation of EPC on treatment with anhydrous EPC, products with a low molecular weight, containing large amounts of propenyl end groups, are also formed. Treatment of the alkaline polymer with an equal amount of polymer obtained in an independent experiment does not increase the degree of unsaturation of the system. However, treatment of the alkaline polymerisation mixture at a ~100% degree of conversion with a fresh portion of the monomer leads to an increase in the degree of unsaturation.[33]

IV. The properties of *N*-(2,3-epoxypropyl)carbazole oligomers

1. Physicochemical properties

The products of the polymerisation of EPC are oligomers with a molecular weight up to 2000, which consist of colourless powders readily soluble in aromatic and chlorinated hydrocarbons, DMF, THF, and acetone and insoluble in alcohols and alkanes.

Depending on the molecular weight, the glass points T_g of the EPC oligomers are in the range 70–105 °C [54,55] and for equal molecular weights are appreciably lower than the T_g for PVCA obtained both by the polymerisation of *N*-vinylcarbazole[56] and by the transvinylation reaction.[57] This can be explained by the increase in the flexibility of the PEPC chain owing to the presence in the macromolecule of ether linkages and the removal of bulky carbazole substituents from the main chain of the oligomer as a result of the introduction of the methylene group.

The dependence of T_g on the weight-average molecular weight M_w for PEPC obtained in the presence of $SnCl_4$ and the $Al(OPr^i)_3-ZnCl_2$ mixture is very pronounced for low values of M_w, becoming less marked for M_w above 2500, and not being manifested at all for still higher values of M_w.[55] When $M_w \simeq 10^4$, one may expect the formation of a thermomechanical segment which depends on the method of synthesis of PEPC.

The products of the cationic polymerisation of EPC (in the presence of $SnCl_4$ or $BF_3.OC_2H_5$) have higher glass points T_g than the polymers with similar M_w obtained in the presence of other catalysts, which has been attributed to intramolecular and intermolecular donor–acceptor interactions between the residues of the catalyst bound covalently to PEPC and the carbazole groups. Another explanation of this finding may be the formation in the first case of cyclic structures, as has been observed for PVCA.[58] Indeed, it has been shown that, in the cationic polymerisation of EPC using $BF_3.OEt_2$, between 31 and 48% of oligomeric cyclic structures are formed.[42] The glass points of the EPC oligomers with molecular weights in the range from 800 to 1800, obtained in the presence of the SN complex, increase from 90 to 100 °C and are almost identical with the T_g of oligomers having the same molecular weights but obtained on treatment with KOH.[54] For similar molecular weights, the T_g of PDBEPC and PNEPC are higher by 10–15 °C than in the case of the unsubstituted PEPC, which is apparently associated with the increase in the polarity of the substituted carbazole groups.

Oligomeric PEPC has been analysed by X-ray diffraction[59] and a study has been made of the relation between its photosemiconducting properties and its phase state. The diffractometer traces of all the oligomers show, regardless of the methods of their synthesis, only an amorphous halo with a maximum at scattering angles $2\theta = 20-21°$ and signs of crystallinity are completely absent. The phase state of the oligomeric PEPC is not affected by the character of the end group (hydroxy-groups, unsaturated groups, and cyclic groups) and also by the heat treatment of the PEPC specimens for 1 h at temperatures up to 150 °C. It has been suggested that PEPC has an atactic molecular structure. It has been shown that the absence of crystallinity of PEPC in anionic polymerisation can be associated with the occurrence, together with the β-dissociation, also of the α-dissociation of the epoxide ring, while in cationic polymerisation it is associated with the formation of cyclic structures, which lead to the breakdown of the structural crystallisation condition.

The physicochemical properties of PEPC have been investigated in order to create thermodynamic foundations for the technology of electrophotographic materials based on it.[60] A study was made of the heat capacity of PEPC ($\overline{M}_n = 1200$) in the temperature range 0–350 K. In the temperature range 320–340 K, the heat capacity increases abruptly under constant pressure by an amount 0.413 J $g^{-1}K^{-1}$, which is associated with the devitrification of the oligomer. The T_g of PEPC determined in this way was 335 K. The heat capacity at room temperature was 1.121 J $g^{-1}K^{-1}$.

The thermal stability of EPC, its oligomer, and PEPC, stabilised by the Santonox-P and Bisalkophen-MCP antioxidants, has been studied by the derivatographic method.[61] It was shown that the ease of the thermo-oxidative degradation in PEPC compared with the monomer indicates the presence in the oligomer of impurities which accelerate this process.

Thin-layer chromatography of the EPC polymerisation products[62] made it possible to discover whether or not the unreacted monomer is present and also to determine the molecular weight distribution in the PEPC. The mechanism of the formation, the molecular weight distribution, and the separation of the oligomeric EPC with $\overline{M}_n$ up to 15000 by gel permeation chromatography have been investigated.[63]

2. Optical and photophysical properties

The study of the electronic spectra of free and sensitised PEPC layers and of the influence of UV radiation on the latter in air, the analysis of the photochemical oxidation products, and also the study of the photochemical reactions in polymers help to elucidate the mechanism of the photophysical phenomena occurring in processes involving the optical recording of information. The electronic absorption and luminescence spectra of PEPC and of its brominated derivatives have been studied[13,20,64–69] both in solution and in thin films. The absorption in PEPC is associated with the presence of carbazole nuclei and is determined by the allowed transitions between the singlet levels of the π electrons. The long-wavelength absorption band in the spectra of EPC oligomers is at 345 nm, while the remaining bands correspond to wavelengths of 295, 262, and 237 nm, the maxima in the absorption spectra of the thin layers undergoing a bathochromic shift by 2–4 nm compared with the maxima in the absorption spectra of the solutions. For the bromo-substituted PEPC oligomers,[69] the long-wavelength absorption band maximum has undergone a bathochromic shift compared with the unsubstituted PEPC, which is associated with the change in the electronic structure of the carbazole chromophore after the introduction of bromine atoms into its nucleus. The influence of structural factors on the formation of CTC in solution by the carbazole fragments of PEPC and its derivatives containing electron-accepting substituents with 2,4,7-trinitro-fluoroenone (TNF), 9-dicyanomethylene-2,4,7-trinitrofluorene (DCMTNF),[70] and triarylpyrylium tetrafluoroborate (TAPS) has been observed.[71,72] It has been found that the broad charge transfer band in the spectra of CTC of PEPC with TNF has $\lambda_{max} = 500$ nm and does not shift after the introduction of substituents into the carbazole nucleus, while the band for the CTC of PEPC with DCMTNF lies in the range 550–625 nm depending on the nature of the substituent. Furthermore, the introduction of electron-accepting substituents into the carbazole nucleus diminishes the equilibrium formation constant of the CTC. Comparison of the stability constants and the enthalpies ΔH of the complexes of PEPC with TAPS, TNF, and 2,4,5,7-tetranitro-fluoroenone (TENF) shows that the TAPS molecules in the CTC exhibit weaker electron-accepting properties.[71]

The luminescence of layers and solutions on irradiation with UV light is characteristic of EPC oligomers. The luminescence spectrum of PEPC depends greatly on the solution concentration. The spectra show maxima at 358 and 386 nm associated with the phosphorescence of the monomeric units and maxima at 408 and 427 nm associated with the emission by excimers,[66,67] the intensity of the glow of which increases with decrease in temperature. The luminescence quantum yield in PEPC at room temperature is $\varphi = 0.25$ and increases with decrease in temperature, which is

apparently associated with the decrease in the probability of non-radiative transitions. As the number of substituents in the carbazole nucleus increases, the emission band maxima in the luminescence spectra undergo a bathochromic shift and for di- and tri-bromo-PEPC consist of a broad band with λ_{max} = 391 and 396 nm respectively, while for tetrabromo-PEPC they are actually located at λ_{max} = 399 nm. The fluorescence spectra of layers of bromo-substituted PEPC with TNF, TENF, and DCMTNF show broad emission bands in the range 500–800 nm associated with the formation of CTC.[67] It is known[73] that in organic semiconductors the carrier generation processes are influenced significantly by the products of photochemical reactions. It has been found that, after exposure to the joint action of oxygen and UV radiation, films of bromo-substituted PEPC undergo photochemical oxidation, which diminishes the fluorescence intensity. Films of poly-tetrabromo-EPC are most sensitive to the action of UV light in air. The decrease in the intensity of the fluorescence emission band in the range 500–800 nm after prolonged UV irradiation (for more than 3 h) has been explained by the decomposition of the CTC and the partial degradation and cross-linking of the oligomer.[67]

On the basis of the study of the products of the photochemical oxidation of various PEPC specimens, attempts have been made to establish the mechanism of this process and its relation with the photosensitivity and the spectroscopic and electrophotographic parameters of layers of EPC oligomers.[74–78] When specimens of PEPC and of its brominated derivatives are UV-irradiated in air, the absorption in the wavelength range 360–600 nm increases, a long-wavelength band appears, and the optical densities of all the absorption bands in the region of the electronic transitions in the carbazole rings diminish, which has been attributed to the formation of carbazole *N*-oxides.[75,76] It has been shown that the intensity of the 1735 cm^{-1} absorption band in the IR spectra of the oligomers obtained in the presence of KOH increases with time and eventually becomes constant when the unsaturated end groups disappear, while the intensity of the 1715 cm^{-1} band increases monotonically.[75,76] Since the absorption bands at 1715 and 1735 cm^{-1} correspond solely to the carbonyl groups, it has been suggested that the photochemical oxidation products may be, together with structures of the ketone type, also quinone imide structures (band at 1715 cm^{-1}), from which units containing several carbonyl groups in the carbonyl nucleus may be formed subsequently. The molecular weight and the degree of polydispersity of the oligomers increase somewhat in highly photochemically oxidised PEPC specimens, which has been explained by the possibility of their cross-linking either via double bonds in the presence of unsaturated end groups or via carbonyl groups in the absence of unsaturation.[76]

Data obtained in studies of the electronic structures and photochemical reactions under the influence of UV irradiation in air of thin PEPC films sensitised by small amounts of added TNF, TENF, DCMTNF, and chloranil (CA) have been published.[77,78] In pure and sensitised PEPC specimens, an increase in absorption (darkening) is observed in the range 350–600 nm, becoming more pronounced as irradiation becomes more prolonged. It has been shown that the highest sensitivity to UV irradiation and hence relatively rapid ageing is exhibited by specimens of pure PEPC whose resistance to irradiation increases by a factor of almost 1.5 after the introduction of 1 mol% of sensitiser. It has also been shown[77,78] that the photochemical oxidation products, formed in the surface layer of the film, have electron-accepting properties and influence significantly the fluorescence intensity of PEPC films. The photochemical oxidation products in the PEPC layers are regarded as effective electron-accepting impurities which play a definite role in the mechanism of the photogeneration of current carriers.[79] The degree of electronic interaction between carbazole groups in photoconductors has been studied by proton and magnetic resonance (^{1}H NMR).[80] An upfield shift of the signal due to the aromatic protons of the carbazole chromophores, characteristic of PVCA, was not observed in the ^{1}H NMR spectra of PEPC solutions. The ^{1}H NMR spectra of PEPC do not differ from those of *N*-ethylcarbazole used as a model compound. A strong electronic interaction between the π-electron systems of the chromophoric nuclei in the ground state has not been observed in solutions of PEPC and of poly(*N*-carbazolylethyl glycidyl ether) by ^{1}H NMR, which has been explained by the greater difference between the carbazole chromophores and by the flexible character of the main chain. It has been suggested that, in solutions of this polyether and of PEPC, the carbazole nuclei can rotate freely about the methylene linkage in contrast to the rigid-chain PVCA.[80]

The manifestation of photosensitivity and the occurrence of a series of photophysical processes in the UV region in PEPC and its derivatives are determined primarily by the presence of the carbazole side group. In the visible region of the spectrum, PEPC does not exhibit photosensitivity.[65] In the early studies, it was already noted[81] that the photosensitivity in carbazole-containing polymers, in particular in PVCA, in the visible region is associated with the formation of donor–acceptor complexes in which the carbazole group functions as the electron donor and the impurity functions as the electron acceptor. It has been found that the photoconductivity of PVCA and of its derivatives is influenced by various electron-donating and electron-accepting additives as well as dyes. It has been shown that a correlation between the photosensitivity and the electron affinity of the sensitiser occurs only in series of electron-accepting compounds with similar π-electron systems. The most effective sensitisers for PVCA and its derivatives are TNF [82] and pyrylium, benzopyrylium, and thiapyrylium salts.[83]

Similar results were obtained in the study of the electrophotographic, optical, and photophysical properties of layers based on PEPC and some of its modified derivatives. In organic PVCA and PEPC semiconductors, there are no bands and hence the ideas of the classical band semiconductors are not applicable to them. In these semiconductors, the carriers apparently move via a jump mechanism, within the framework of which attempts have been made to account for the mechanism of the transport and photogeneration of charge carriers.[84] The photogeneration mechanism is closely related to the mechanism of the sensitisation of these semiconductors, i.e. to the energy transfer from the excited sensitiser molecule in the organic semiconductor and with the generation of a charge transfer state. The mechanism of the charge generation in layers of PEPC photochemically oxidised to different extents under electrophotographic conditions and of the influence on the photosensitivity of such layers by impurities of different kinds (initial carbazole, the monomer, the catalyst residue, and the solvent) has been described.[76] It has been established that the layers obtained from the more oxidised PEPC also have higher photosensitivities. The primary photophysical processes,[85–92] the photogeneration quantum yields,[93–98] and the drift mobilities of the charge carriers[99–104] in pure PEPC layers and PEPC layers sensitised by various additives have been investigated.

The study of the stationary photoconductivity and fluorescence, taking into account the influence on them by an external magnetic field, in PEPC layers with added dyes[87,88,91] has shown that excited charge transfer complexes participate in the current carrier generation

process both in the intrinsing absorption region and in the sensitisation region. The dissociation of the charge transfer complexes is facilitated by the external electric field and by the exciplexes formed by the interaction of the excited state of the dye with the chromophoric group of the oligomer. The dissociation of the complex with formation of current carriers takes place in its vibrationally relaxed state. The study of the characteristic features of the volume photoconductivity in thin PEPC layers sensitised by TNF[88] permitted a conclusion concerning the nature of the appearance of photogenerated current carriers in the region of the CTC absorption. Very interesting results have been obtained by studying and comparing the photophysical properties of PEPC and its brominated derivatives sensitised by different electron acceptors.[90–92] Pure layers of brominated PEPC are less photosensitive than the non-brominated PEPC in the UV region of the spectrum for positive charges and for an electric field strength of 5×10^7 V cm^{-1}. It was found previously[75–78] that, under real operating conditions, the photosensitivity of layers of PEPC and its derivatives is influenced significantly by UV radiation and oxygen (photochemical oxidation process) and that a decrease in the degree of oxidation of oligomers reduces the photosensitivity and the quantum yields of the generation of charge carriers in the UV region of the spectrum.[76]

The oxidation and photochemical oxidation of the carbazole group with formation of electron accepting quinone imide structures, which are ultimately responsible for the decrease in photosensitivity, are hindered in brominated PEPC. Predominately singlet excitons are responsible for the generation of charge carriers in brominated PEPC. The study of the quantum yield β[93–96,98] and of the characteristic features of the photogeneration and recombination of current carriers[97] in pure PEPC and PEPC sensitised by different additives has shown that, when pyrylium salts are used as sensitisers, the yield β in PEPC layers for an electric field strength $E \simeq 10^6$ V cm^{-1} increases to 0.36, whereas for the unsensitised specimen $\beta = 2.7 \times 10^{-2}$. The power dependence of β on E with an exponent of 1.2×3.3, depending on the wavelength and the nature of the sensitiser, has been demonstrated.[95,98] For PEPC layers with a 20% content of a binder and sensitised with 3 mol% of TNF, the power exponent increases from 2.3 to 3.3 when the temperature is reduced from +50 to −60 °C for $E = 10^6$ V cm^{-1} at an exciting light wavelength $\lambda = 295$ nm. In sensitised PEPC layers, the activation energy for the photogeneration of carriers (ΔE) depends only slightly on the exciting light wavelength and increases from 0.039 to 0.13 eV with decrease in the electric field strength from 1.6×10^6 to 4.0×10^5 V cm^{-1}. The increase in β with increase in the TNF concentration is caused by the improvement of electron transfer conditions.[96]

The characteristic features of the drift mobility of charge carriers have been investigated in PEPC[65,99–103] and also in a mixture of PEPC with PVCA.[104] It has been established[100,101] that in PEPC layers electrons remain stationary and the drift mobility of the majority current carriers (holes) depends to a large extent on the temperature and the electric field strength, reaching 7.5×10^{-6} cm^{2}V^{-1}s^{-1} for layers 1.5–4.5 μm thick and $E = 5 \times 10^5$ V cm^{-1}. The distances between the carbazole rings in pure PEPC are 6.8 Å, which is greater by 0.4 Å than in PVCA.[105] Evidently the increase in the drift mobility in PEPC relative to that in PVCA can be explained by the decrease in the distance between the carbazole nuclei in PEPC as a consequence of their displacement from the equilibrium position by 2–3 Å in the direction in which the electric field strength acts with increase in the probability of the transfer of the carrier between them.[100] The drift mobility of holes in PEPC layers diminishes with increase in the acceptor (TNF) concentration. After the introduction of 10 mol% and more of the acceptor, the drift mobility of the electrons can be measured. It becomes approximately equal to the mobility of holes in the presence of 50 mol% of the acceptor. The activation energies for the drift mobility in PEPC layers for electric field strengths of 4.5×10^5 and 1.5×10^5 V cm^{-1} are respectively 0.24 and 0.32 Ev.

The photoconductivity of EPC oligomers increases significantly and is manifested over a wider spectral range in the presence of optical and chemical sensitisers. Optical sensitisation is observed after the introduction of dyes into the oligomer at low concentrations as a result of the absorption of light by the dye molecules in the visible region, while chemical sensitisation is effected after the introduction of electron acceptors, which usually absorb in the UV region of the spectrum. The sensitisation of the photosensitivity of EPC oligomers by added organic dyes,[106–121] electron acceptors,[122–126] and compounds specially synthesised for the sensitisation of PEPC[127–132] has been investigated.

The study of the characteristic features and mechanism of the sensitisation of EPC oligomers by dyes,[109,111,113,114,116] nitrofluorenones,[122,124] and pyrylium salts[113,118,120] has shown that the effectiveness of the sensitisation of PEPC by TNF acyloximes[124] and arylpyrylium salts with perchlorate and tetrafluoroborate anions[114,119] greatly exceeds that of the sensitisation by TNF and TENF both in the intrinsic absorption region and in the long-wavelength region. The strong sensitising effect of pyrylium salts has been explained by the ability of pyrylium cations to bind in PEPC electron-donating impurities which generate centres for the adhesion of holes.[114] The low effectiveness of the sensitisation of PEPC by certain dyes (rhodamine 6G) compared with pyrylium salts has been attributed to the fact that aromatic amino-groups in the dye molecules create deep carrier capture centres in the PEPC layers. However, when up to 1 wt.% of boron trifluoride etherate is introduced into the system, the photosensitivity increases fivefold and reaches the level for pyrylium salts. The increase in the sensitising capacity of the above dyes after the introduction of Lewis acids has been explained by the binding of the amino-groups in the dye molecules and hence by the decrease in the concentration of deep carrier capture centres.

3. Electrical properties

The study of the electrical properties of PEPC and its complexes with various additives helps to obtain additional information for a deeper understanding of photoelectric processes, for the estimation of molecular parameters, and for the elucidation of the mechanism of the polarisation in the dark discharge of electrophotographic layers.

Fairly numerous studies have been devoted to the electrophysical properties of polymers based on *N*-vinylcarbazole and its derivatives.[1,2] However, the available literature data on the electrical properties of oligomers based on EPC are extremely scanty.

The electrical properties of free PEPC films and PEPC films sensitised by low-molecular-weight additives have been investigated.[133–135] The dielectric properties, polarisation effects, and their temperature dependence have been described.[136–138] In the study of the temperature dependence of the parameters of a galvanic cell in the Au–PEPC–Al system, ionic conduction was observed in PEPC. It was shown that the Au–PEPC–Al system forms a galvanic cell, whose e.m.f. is $E_0 = 150$ mV in the initial instant, the Au electrode being charged positively. It has been assumed that the e.m.f. in the

above system is due to oxidation-reduction reactions on the metallic electrodes and indicates the presence of an ionic component of the electrical conductivity, whose nature is associated with low-molecular-weight impurities or with the dissociation of polymer macromolecules in the solvent.[133]

The dependence of the dark current on the potential for PEPC films with added TNF obeys Ohm's law up to an electrical field strength of 10^3 V cm^{-1}. For higher field strengths, there is a break in the voltage–current characteristic and a power dependence of the current I on the applied potential U is observed with an exponent of 2.2. The non-linearity of the voltage–current characteristic is attributed to the injection of charge carriers from the electrode into the PEPC, which establishes a regime in which the current is limited by the space charge.[134] Measurement of the electrical characteristics of the conducting PEPC oligomer and of its complex with tetracyanoquinodimethane (TCQDM) showed that in the region of high potentials the voltage–current characteristics of both the pure oligomer and of its complex are non-linear and exhibit hysteresis. It has been demonstrated by the thermocurrent method that the majority charge carriers in PEPC are electrons, while in the PEPC–TCQDM complex they are holes with concentrations of 8.5×10^{13} and 1.4×10^{14} cm^{-3} respectively.[135] It has been observed that, depending on the conditions in the preparation of the specimen, the real component of the dielectric constant at room temperature is 2.7–3.1 and is associated mainly with electronic polarisation.[138] In layers of the pure EPC oligomer, the tangent of the dielectric losses angle ($\tan\delta$) has a distinct maximum above the glass point; the maximum shifts towards higher temperatures with increase in the molecular weight and with increase in the frequency of the electric field f, the $\tan\delta$ curve becoming broader under these conditions.

The effective activation energy E, obtained from the temperature dependence of the maximum value of $\tan\delta$, amounts to 2.4 eV for the oligomer with $\overline{M}_n$ = 750 and 3.2 eV for PEPC with $\overline{M}_n$ = 1570.[138] The static dielectric constant ε_s of PEPC layers, determined from the Cole–Cole diagram, is 7.84. It has been suggested that ε_s of PEPC layers, like that of PVCA layers,[136] is determined by the polarisation of the carbazole groups.[137]

The dielectric properties and structure of PEPC irradiated with UV light and γ-quanta in the presence of oxygen have been investigated.[139] A significant influence of different types of radiation on the dielectric parameters of PEPC has been observed, which is associated with the structural changes occurring in the polymer.

When PEPC was irradiated with UV light for periods up to 30 min, a sharp decrease in $\tan\delta$ and ε' was observed. With increase in the duration of irradiation, $\tan\delta$ and ε' rise to a maximum and then diminish monotonically until the attainment of a plateau after irradiation for 8 h. The decrease in $\tan\delta$ and ε' in the initial stage of the photochemical process has been explained by a significant contribution of peroxy-radicals, formed during the irradiation process, to the depolarisation of PEPC. The peroxy-radicals, which have a large dipole moment,[140] interact with dipoles and some of the dipoles, whose interaction energy with the charge field is greater than the energy of their interaction with the applied field, are not involved in the relaxation. This diminishes $\tan\delta$ and ε' as a consequence of the decrease in the concentration of the dipoles acting in the relaxation process. The increase in the dielectric parameters has been attributed to the formation of stable carbonyl groups.

The temperature and field dependences of ε' and $\tan\delta$ for layers of pure PEPC and its complex with TNF have been investigated.[141] It has been shown that the character of the temperature dependence of ε' for the PEPC and EPPC–TNF layers is identical but in the complex ε' is somewhat higher than in the pure oligomer, which has been explained by the contribution of the TNF molecule to the polarisation of the system and also by the electronic thermal polarisation due to weakly bound electrons arising in the complex formation process.

The electrical conductivity of films of PEPC and the copolymer of EPC with 5% of BGE (where BGE = butyl glycidyl ether) has been investigated by the method of thermostimulated currents in the Al–PEPC–SnO_2, Al–(EPC + 5% BGE)–SnO_2, and Al–PVB–(EPC + 5% BGE)–SnO_2 sandwich structures (where PVB represents a layer of a dielectric–polyvinylbutyral).[142] It was observed that, in the ranges 213–263 K and $E = 10^7$–10^8 V m^{-1}, a saturation current regime obtains in the PEPC and PEPC + 5% BGE films in which the current varies linearly with the hole generation efficiency within the bulk of the film (having a thermal field character) and with the film thickness, while in the range 273–313 K the electrical conductivity is determined by the generation and drift of ions.

The nature of the dark electrical conductivity of freshly cast and dried PEPC layers has been investigated by the method involving the dark decrease in potential.[143] Measurements were made of the time variation of the capacitance, ε_s, the charging current in long electrisation stages, and the reduction potential of the specimens with the applied potential and on subsequent short-circuiting. The results indicate the operation of several electrical conduction mechanisms in both fresh and stabilised PEPC layers. A two-layer model of the dark electrical conductivity in PEPC, which explains the polarisation phenomena in this material and describes the changes in its properties on stabilisation, has been proposed.

The electrical conductivity of a composition based on PEPC with a filler comprising a triphenylmethylphosphonium–TCQDM radical-ion salt has been investigated.[144] The electrical conductivity of the composition is determined by the contact conductivity at the boundary between the particles of the filler and the binder. The contact conductivity is non-linear and is of the semiconducting type. The activation energy for the electrical conduction in the composition exceeds E_σ for the filler and the binder. It has been suggested that the electrical conduction is effected by the emission of electrons from part of the filler and their activated transport in the layer of the binder.

4. Practical applications of carbazole-containing polymers

The high photoconductivity of carbazole-containing polymers with added organic dyes (OD) and with electron-accepting compounds (EAC) permits their use as photosemiconducting materials for the preparation of electrophotographic layers (EPL) designed for microfilming, the recording of information by the photothermoplastic method, and for the manufacture of multicolour electrophotographic images and slides.[1]

Studies on the possibility of creating EPL and other non-silver layers on the basis of polymeric photoconductors are being widely prosecuted at the present time in the USSR, Japan, the Federal Republic of Germany, the USA, and other countries. Organic compounds belonging to a wide variety of different classes are used as light-sensitive media suitable for electrophotographic processes.[145–148]

Many studies have been devoted to the use in EPL of polymers containing in their structure the carbazole nucleus, for example, polyallylcarbazole, polypropenylcarbazole, poly-*N*-acryloylcarbazole, and their derivatives, as well as 1,4-divinylcarbazole polymers and copolymers.[147] However, PVCA is one of the most thoroughly investigated carbazole-containing polymeric photosemiconductors which is widely used in electrophotography. Oligomeric PVCA is used in the USSR for the manufacture of electrophotographic and photothermoplastic materials.[149–151]

Photothermoplastic layers must be transparent in the visible part of the spectrum and elastic and must have a smooth surface and resistivities in the solid and softened states of $10^{14}-10^{15}$ and $10^{10}-10^{11}$ Ωcm. They must be effectively charged in the dark, must possess thermoplastic properties and a glass point in the range 50–80 °C,[56,152] and must not break on repeated bending and on being immersed in the carrier liquid of the electrophotographic developer and on cooling (to a temperature below –60 °C).[153] In this respect the EPL based on the EPC oligomers[40] are believed to be extremely promising in applications which include the formation of a multicolour electrophotographic image.[154]

Electrophotographic films based on PEPC have been investigated[106] and a detailed study has been made of the photoelectric properties of PEPC and its possible applications have been defined. The sensitisation of PEPC by various electron-accepting compounds and organic dyes has been studied and the most effective sensitisers for this purpose have been discovered. It has been shown that the introduction of electron-accepting compounds and of an organic dye into the PEPC layer alters the conditions in the generation and transport of carriers. PEPC layers sensitised by polynitrofluoroenones are effectively charged, both positively and negatively, and exhibit a weak dark relaxation of the potential and a zero residual potential, while PEPC layers sensitised by organic dyes exhibit a fairly pronounced dark relaxation of the potential.

Organic electrophotographic films (OEPF) of three types have been developed on the basis of PEPC:[153] OEPF-M of type T-1 for the generation of images in accordance with the positive–positive or negative–positive scheme with positive charging, OEPF-M of type T-2 in accordance with the positive–positive scheme with negative charging, and OEPF-M of type T-3 for the preparation of positive images in accordance with the positive–positive (negative charging) or negative–positive (positive charging) scheme. In an OEPF frame, it is possible to form up to eight images and by developing them with different toners it is possible to obtain multicolour images (resolving capacity 300 lines mm^{-1}) which are stable under an illumination of 5×10^4 lx and at a temperature of 55 °C for 24 h.

Panchromatic EPL for colour images have been developed on the basis of PEPC to which 1–15 mol% of TENF has been added.[154] It has been shown that, with increase in the TENF content to 10 mol%, the photosensitivity increases almost linearly. A further increase in the acceptor concentration does not increase the photosensitivity and in the blue region of the spectrum actually reduces it. An increase in the TEMF content leads to a slight diminution of the positive potential in the dark (from 3 to 5%), while the dark decrease in the negative potential is constant and amounts to 6%. The dark decrease in potential rises to 8–10% when the degree of illumination is high (5×10^3 lx in 1 min).

It is known that, when EPL based on PEPC are used under real conditions, the working parameters of the photosemiconductor are influenced by various external factors (UV irradiation, oxygen, temperature, etc.), which lead to photochemical oxidation and other changes. Photochemical oxidation processes can be regarded to some extent as model reactions in relation to the real operating conditions of photothermoplastic materials in electrophotographic and photothermoplastic regimes.

By studying the influence of UV irradiation on the electrophotographic sensitivity (EPS) and diffraction efficiency (DE) of EPL, it is possible to obtain definite information about the characteristics of the degradation of these materials.[78]

The most significant changes in photosensitivity are observed after brief UV irradiation (up to 1 h): there is initially a sharp decrease in the EPS and then a slight increase. The attainment of an EPS plateau as a function of the duration of irradiation is observed for exposures ranging from 1 to 10 h. It has been noted that the character of the variation of EPS during UV irradiation is independent of the type of electron acceptors introduced into the PEPC. Reactions involving carbazole nuclei play the main role in the changes in EPS during photochemical oxidation. Brief UV irradiation does not entail a change in the diffraction efficiency of photothermoplastic carriers (PTC) based on PEPC + 2% TNF. The maximum diffraction efficiency, observed for exposures of 0.1–0.15 mJ cm^{-2} is 20–22% for carriers based on PEPC + 2% TNF and PEPC + 2% CA and 16–18% for PEPC + 5% CA. For carriers with a high TNF concentration (5% and above) and also for DCMTNF (3% and above), holographic recording is hardly feasible.

In the PEPC spectra, the long-wavelength absorption band and the first photosensitivity maximum are determined by the carbazole chromophoric group and are in the UV region of the spectrum at $\lambda = 345$ nm.[119] In order to impart to the organic conductor sensitivity in the visible region of the spectrum, spectral sensitisation by organic dyes or electron-accepting compounds, which form charge-transfer complexes with PEPC, is employed.[106,111,119,122,155]

Table 2. The influence of the nature and concentration of the acceptor on the photosensitivity of PEPC.

Acceptor	Photosensitivity ($E_0 = 75$ V μm^{-1}) at different acceptor concentrations (mol%), 10^3 lx^{-1} s^{-1}					
	0.1	0.5	1.0	2.0	5.0	10.0
9-Fluorenone	0.04	0.045	0.04	0.044	0.04	0.12
DNF	0.08	0.22	0.5	0.5	0.8	2.9
TNF	0.14	0.5	0.8	1.15	2.5	4.2
TENF	0.3	0.6	1.12	3.1	4.0	7.2

The xanthene dye rhodamine 6 G is regarded as a highly effective sensitiser (in relation to electrophotographic sensitivity) of PEPC EPL among organic dyes,[110,111] while among electron-accepting compounds polynitrofluorenones (TNF and TENF) are effective.[106,122]

The dependence of the photosensitivity of PEPC layers on the content of rhodamine 6 G in the layer, shows that the highest photosensitivity is that of PEPC layers containing 0.9 mol% of the dye.[111] At $\lambda = 540$ nm, the photosensitivity of this composition reaches 29 m^2J^{-1}.

Table 2 presents the photosensitivites of positively charged PEPC layers, sensitised by nitrofluorenones, on illumination with white light[122] (DNF = 2,7-dinitrofluorenone).

The decrease in potential in the dark over a period of 1 min at E_0 = 75 V μm^{-1} does not exceed 5%. The absence of the photosensitivity of the unsensitised layers in the presence of a negative charge shows that holes but not electrons are mobile in PEPC. In the PEPC + 1 mol% TNF or TENF compositions, photosensitivity appears also in the presence of a negative charge. At such concentrations of electron-accepting compounds, electrons also become mobile. The introduction of organic dyes and electron-accepting compounds into PEPC results both in an increase in the electrophotographic sensitivity in the intrinsic absorption band of the oligomer and in the expansion of the spectral range of the photosensitivity up to 650 nm.

Measurements have been made of the dependence of the photosensitivity of PEPC layers on the amount of pyrylium salt introduced and the distributions of the spectral sensitivity of the layers in the wavelength range 250–650 nm have been investigated.[119] In order to sensitise PEPC, pyrylium salts with different substituents in the 2-, 4-, and 6-positions in the pyrylium ring, comprising perchlorate and tetrafluoroborate anions, have been studied.

Among the pyrylium salts investigated, the best sensitisers of PEPC layers are 4,6-diphenyl-2-*p*-tolylpyrylium perchlorate (D1), 2,6-dianisyl-4-phenylpyrylium perchlorate (D2), 2,6-dianisylpyrylium perchlorate (D3), 4-anisyl-2,6-dinaphthylpyrylium tetrafluoroborate (E1), 2-anisyl-4,6-diphenylpyrylium tetrafluoroborate (E2), and 2,6-dianisyl-4-phenylpyrylium tetrafluoroborate (E3).

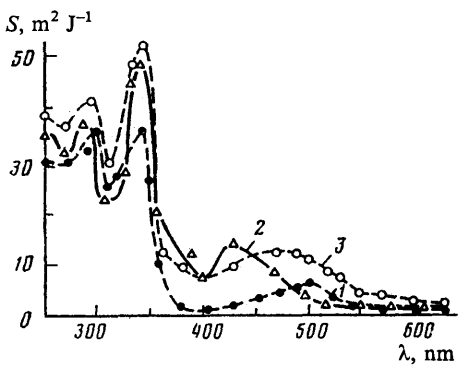


Figure 1. Distribution of the spectral sensitivity (S) of PEPC layers sensitised by the pyrylium salts D3 (curve *1*), D1 (curve *2*), D2 (curve *3*); $E = 5 \times 10^7$ V m^{-1}, c = 1 mol%, positive charge.[119]

The sensitivity of the unsensitised PEPC layers at λ = 295 nm for $E = 5 \times 10^7$ V m^{-1} is about 2 $m^2 J^{-1}$. A small amount of pyrylium salts greatly increases the photosensitivity of PEPC layers. It has been shown that the maximum concentration for the majority of pyrylium salts is 3–5 mol% relative to the PEPC monomeric unit. However, in the presence of 1–3 mol% of the sensitiser, saturation of the photosensitivity is observed and, on further increase in the content of the pyrylium salt, the photosensitivity begins to fall. The decrease in photosensitivity is explained by the formation of a negative space charge which reduces the rate of the photoinduced decrease in the potential.

Figs. 1 and 2 present curves for the distribution of the spectral sensitivity of PEPC layers containing 1 mol% of pyrylium salts. It is seen from the figures that pyrylium salts having a long-wavelength absorption maximum in the visible part of the spectrum have a much higher sensitising effectiveness than polynitrofluorenones and rhodamine 6G.

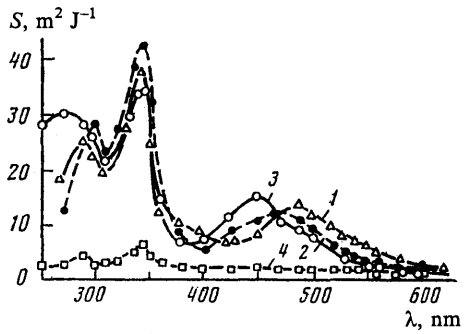


Figure 2. Distribution of the spectral sensitivity (S) of PEPC layers sensitised by pyrylium salts E3 (curve *1*), E2 (curve *2*), and E1 (curve *3*) (c = 1 mol%) and by TNF (curve *4*) (c = 3 mol%); $E = 5 \times 10^7$ V m^{-1}, positive charge.[119]

It is known that low-molecular-weight impurities, polymer end groups, triplet oxygen, polymer oxidation and photochemical oxidation products, and specific local conformations of the macromolecules can serve as deep centres for the capture of mobile holes in carbazole-containing photosemiconductors.[156–158] Low-molecular-weight ionogenic impurities can influence the visualisation of a latent electrophotographic image in the electrophotographic layer, which results in the appearance of different defects and in the diffuseness of information symbols on the developed image. The conditions in the synthesis of PEPC influence significantly the residual potential (U_{res}) of its electrophotographic layer. The main cause of the high value of U_{res} in PEPC layers is traces of the anionic catalyst and of electron-donating substances with a lower ionisation potential than that of the carbazole chromophore.[118,157]

The study of the photosensitivity and U_{res} of PEPC specimens obtained by anionic and cationic polymerisation and sensitised by TNF and 2,4,6-triphenylpyrylium perchlorate, introduced in amounts of 0.5 and 3 mol% respectively and 0.1 and 0.5 mol% respectively into a monomeric unit of the oligomer, showed that PEPC specimens with a low U_{res} are sensitised more effectively in both the UV and visible parts of the spectrum.[157] The residual potassium hydroxide decomposes the pyrylium sensitisers in the PEPC layers.

At the present time, the PEPC used for the preparation of electrophotographic layers is obtained by the anionic polymerisation of EPC in the presence of potassium hydroxide followed by treatment of the product with acetic acid.[157] In order to reduce U_{res}, the PEPC should be carefully freed from technological impurities, including the catalyst, before the preparation of the electrophotographic layer.

Electrophotographic layers based on industrial PEPC, purified by adsorption, chromatographic, and ion-exchange methods, have been investigated.[158] It has been shown that the greatest decrease in the residual potential of the PEPC electrophotographic layer is obtained when solutions of PEPC in polar solvents are treated with activated charcoal and by passing its solutions through layers of Al_2O_3 or silica gel.

The development of electrophotography imposes stringent requirements on the electrophotographic microfilming apparatus for the representation and replication of information. This suggests the use of semiconducting systems with improved electrophotographic properties.[159]

One of the ways of improving electrophotographic properties of layers based on PEPC is its chemical modification.[89]

In order to prepare layers with an improved electrophotographic sensitivity, brominated PEPC, sensitised by TNF and pyrylium salts, can be used as the photosemiconductor. Brominated PEPC layers sensitised by TNF and pyrylium salts are more photosensitive than the analogous PEPC layers.[89,120,121] This is especially appreciable in the case where PEPC is sensitised by pyrylium salts. The pyrylium cation, which has an exceptionally high electron affinity, ensures electron transfer over long distances from bromocarbazolyl to the pyrylium salt, which leads to an appreciable separation of the charges of the ion pair and to effective dissociation of the electron donor–electron acceptor complex in the electric field with formation of a mobile hole.

The characteristic features and the mechanism of the dark charging processes[160–164] and photocharging processes[165–169] involving pure and sensitised PEPC electrophotographic layers have been investigated. The influence of luminescence on the latent electrophotographic image[170,171] and also of prolonged illumination on the optical, photoelectric, and thermomechanical properties of electrophotographic information carriers (EPIC), prepared on the basis of PEPC,[172] have been investigated. As a result of photochemical reactions, on irradiation with UV light the absorption by electrophotographic information carriers increases in the visible region, the photosensitivity falls, and the rate of discharge in the dark increases. Owing to the impairment of thermomechanical properties, cracking on bending is then observed which precludes photothermoplastic recording. The removal from the spectrum of the UV lamp of radiation at wavelengths less than 400 nm makes it possible to eliminate effects associated with the light-induced ageing of electrophotographic information carriers.

PEPC layers with added TNF have been used to prepare photoelectric converters[173,174] and a varistor.[175] On illumination of a "sandwich" cell with a photosensitive PEPC layer to which 0.5–3.0 wt.% of TNF had been added by light from an incandescent lamp, a photo-e.m.f. equal to 0.6 V was generated between the electrodes for an incident light energy of 20 mW cm^{-2}.[174] The short-circuit photocurrent was in the range 0.1–0.5 μA cm^{-2}. The elucidation of the nature of the photo-e.m.f., in particular the character of the transitions at the aluminium–photoconductor and photoconductor–aquadag contact as well as the estimation of the yield of the diffusion photo-e.m.f. (Dember's e.m.f.) requires further studies. The data obtained have shown that the photovoltaic effect is sufficiently large to suggest that PEPC is a promising material for the manufacture of photocells based on it.

The photocells based on PEPC[173,174] and PVCA[176,177] known at the present time have low efficiencies but their appreciable increase may be expected when the optimum metallic electrode–polymer combination has been selected and also after the development of a technology for the preparation of ultrathin uniform films with a high electrical conductivity.

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The study of the polymerisation of epoxypropylcarbazoles in the presence of various catalysts indicates its very effective occurrence under the influence of anionic catalysts. The use of potassium hydroxide as the catalyst is apparently most suitable as regards the technological aspects of the process. In view of the favourable disposition of carbazole side substituents and the presence of ether linkages in the main chain, EPC oligomers have effective physicochemical and photoelectric properties which permit their use in electrophotography and also in the thermoplastic recording of information.

The basic data on the electrical, optical, dielectric, and photovoltaic properties of carbazole-containing polymers and charge-transfer complexes have now been obtained. Electrophotographic layers used for microfilming, photothermoplastic devices, and the recording of information have now been produced on the basis of carbazole-containing polymers and their derivatives with different acceptors. Studies in this field are extremely promising and are being prosecuted in many world laboratories. The first polymeric photocells based on carbazole-containing polymers have already been created, although they still have low efficiencies. However, the simplicity of their preparation and the low cost of the initial materials have stimulated the development of research into the synthesis of new photoconducting polymers in order to manufacture highly efficient photoelectric cells.

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The improvement of oxidation catalysts

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ABSTRACT. The mechanism of the action of additives introduced into oxide catalysts and silver to increase their activity and selectivity in the oxidation of various organic substances has been examined. Additives can change the kinetic parameters of a process (the rate and activation energy of the reaction) and influence the reaction mechanism by their effect on the structure of the surface compounds and on the energy of the bonds which they form with the surface. The modification of the catalysts gives new compounds (both in the bulk and on the surface), leading to the production of new active centres. The action of additives introduced into multicomponent oxide catalytic systems, and various aspects of their modification by acidic and alkaline additives, have been discussed.

The bibliography contains 62 references.

Contents

I. Introduction 440
II. The influence of additives on the structure and phase composition of catalysts 441
III. The influence of additives on the state of oxygen in oxide catalysts 443
IV. The modification of catalysts by acidic and alkaline additives 445
V. Summary 447

I. Introduction

The efficiency of catalysts is determined by two parameters—the degree of conversion of the starting materials and the selectivity of their conversion into the required products. One of the principal methods for controlling these parameters is by introducing various additives into the catalyst.

Previously, on the basis of the chemical properties of the materials, two types of additive were distinguished: promoters, which increase the activity of catalysts, and poisons, which decrease the activity.[1]

In the period 1940–1950, the study of the extensive oxidation of hydrocarbons on various oxide catalysts and platinum revealed a new phenomenon: the same additive, introduced into a catalyst, may have a promoting or a poisoning effect on the activity of the catalyst, depending on its concentration in the solid.[2–4] It was suggested that the effect ot additives on the properties of catalysts should be described as their modification. The two-fold action of additives was attributed to the change in the same sense in the activation energy and the pre-exponential factor (Fig. 1). This led to an extremal dependence of the reaction rate on the additive concentration (Fig. 2). The phenomenon of catalyst modification was found to be characteristic of not only extensive but also partial oxidation.[5,6] Thus the introduction of additives into copper oxide CuO, a catalyst for the oxidation of propylene to acrolein, brings about the change in the rate and activation energy of formation of the products characteristic of modification. When lithium ions are added to copper oxide, the energy of formation of acrolein changes from 12 kcal mol^{-1} to 22 kcal mol^{-1}, and that of CO_2 from 26 kcal mol^{-1} to 16 kcal mol^{-1}. The pre-exponential factor increases regularly in the order CuO + Li < CuO + PO_4^{3-} < CuO < CuO + Sb^{3+}, from 10^{17} to 10^{22}.

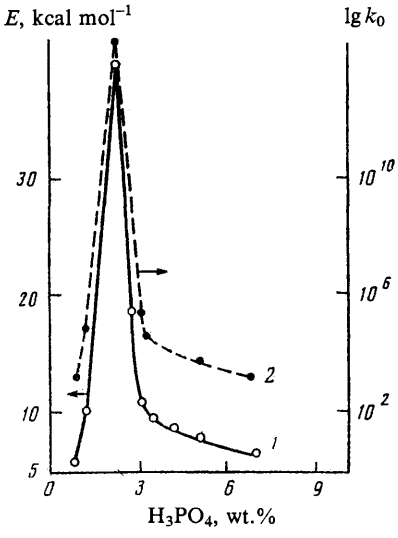


Figure 1. The influence of added H_3PO_4 on the activity of the $MgCr_2O_4$ catalyst in the extensive oxidation of iso-octane: *1*, change in the activation energy; *2*, change in the pre-exponential factor.[3]

Further studies of the control of the conversion and selectivity of oxidation processes showed, however, that these explanations are inadequate. Additives may react with the basic catalyst matrix to form solid solutions and new compounds, and hence increase the number of phases in the catalyst. The effect of these impurities is not limited to changing the phase composition of the catalyst; as a result of the change in the structure, they also influence the probability of electron transitions between the elements in the solid. The rearrangement of the catalyst structure, leading to changes in

the bulk characteristics, also lead to changes in the surface; the additives also take part in the production of the active centres on which the catalytic reaction takes place.

The introduction of additives has produced highly selective catalytic systems used in industry, but the additives have been selected empirically, since the multifunctional character of their action makes it difficult to determine the basic principles of the selection of modifiers for increasing the efficiency of catalysts.

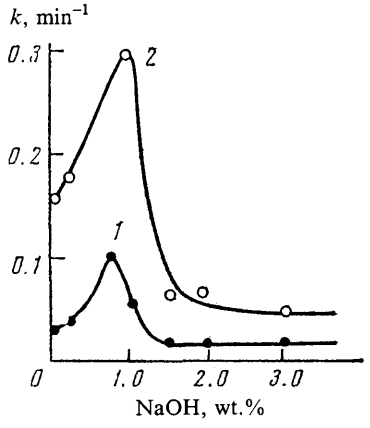


Figure 2. Influence of added NaOH on the rate constant of the oxidation of iso-octane on tungsten oxide at 320 °C (*1*) and 420 °C (*2*).[4]

The accumulated experimental data on modification have not been fully reviewed. A review[8] was published in 1987, dealing with the promotion of various metallic and oxide catalysts for the Fischer–Tropsch synthesis, the hydrogenation of CO, etc., but the nature of the modifying action of the additives introduced into a large number of oxidation catalysts was not examined systematically.

Attempts have been made to explain the mechanism of the modification of catalysts using various theories of catalysis. In the period 1950–1960, Vol'kenshtein,[9] who developed the electronic theory of catalysis, explained the mechanism of the modification of semiconducting oxide catalysts in terms of the band model, attributing it to a change in the position of the Fermi level in the crystals. According to these ideas, additives can change the electronic properties of the crystal in the bulk and on the surface. The catalytic activity of specimens should therefore be compared with the electronic characteristics of the solid, for example the electrical conductivity or the work function. The introduction of donor or acceptor additives changes the position of the Fermi level and decreases the degree of coverage of the catalyst surface by the reagents, which become charged on adsorption (electron acceptors or donors), and this may even lead to a change in the limiting stage of the process and its rate. A large number of papers have been published on the relationship between the electrical conductivity and the work function in the oxidation of various substances on oxide semiconductors.[5] The sign of the charge on a given impurity may be different in the bulk and on the surface of an oxide, however. The electronic characteristics of the impurities in a solid and their influence on a reaction rate may be different, depending on their distribution. It is therefore impossible to establish the mechanism of the varied action of additives by examining only the electronic properties of semiconducting oxides.

In the case of metals, it is considered that the additives and reagents on their surface form charged dipoles, whose electrostatic interaction changes the degree of covering of the surface by the reagents and hence influences the reaction rate.

The study of the modification of silver by additives which are electron donors or acceptors has shown,[5] however, that the mechanism of action of these additives cannot be explained entirely in terms of the interaction of dipoles. The change in the work function when silver is modified cannot be responsible for the change in the activity of the catalyst or the selectivity of the process, and is only an "indicator" of the change in the properties of the surface of the solid. When potassium or halogen ions are introduced into silver, the additive migrates into the bulk, dissolving in its lattice with the formation of microcrystals. The change in the work function is merely a reflection of these processes, and cannot influence the selectivity of catalytic reactions.[10,11]

To determine the mechanism of the action of additives on the properties of catalysts, it is necessary first to study their structure and phase composition, the mobility of oxygen in them, and their acid–base properties.

Of the large number of modified catalysts, various simple and complex oxide systems and one metallic catalyst, namely silver, are examined in the present review.

II. The influence of additives on the structure and phase composition of catalysts

1. Simple metal oxides

Additives are introduced into catalysts in different ways: during the preparation of the basic matrix or by adsorption on the surface of a prepared catalyst. Depending on the method of introduction, the additives may be distributed in different ways in the bulk of the catalyst and on its surface. This may lead to variations in phase composition, which are examined here for the case of a vanadium oxide catalyst.

As a consequence of the characteristics of its structure, vanadium pentoxide reacts readily with foreign metal ions to give vanadium bronzes, that is non-stoichiometric double oxides with the general formula A_xBO_3, showing characteristic semiconducting or metallic conductivity.[12,13] The formation of bronzes can be described as the result of the introduction of foreign atoms or ions into the main lattice. The metal A, entering the lattice, occupies some of the free sites and has no influence on the structure of the main oxide. The introduction of A leads to the production of an impurity level in the band gap of BO_3 below the conductivity band or in the actual band, which is "populated" by electrons of the metal A. Vanadium bronzes are formed particularly readily with the alkali metals and silver. In addition, for the oxidation of aromatic hydrocarbons to aldehydes, use is made of vanadium–molybdenum oxide systems consisting of a solid solution of MoO_3 in V_2O_5 (V : Mo = 1 : 0.27) containing added silver and copper ions. The study of these catalysts by X-ray diffraction, infrared spectroscopy, and EPR has detected the formation of bronzes with vanadium ions in different arrangements. The production of these structures leads to a change in the rate of oxidation of hydrocarbons. According to Volkov and Novak,[13] the diffusion coefficient of oxygen, which is 10^{-8} cm^2 s^{-1} in

V_2O_5, is lower by a factor of 10^2 in the bronzes, due to the presence in the structure of the latter of cavities through which oxygen, the principal component of oxidation processes, moves readily.

To obtain effective oxidation catalysts, vanadium pentoxide is added in different concentrations to MoO_3 and other oxides; the catalytic activity and selectivity depend significantly on the vanadium concentration in the specimen.

According to Andrushkevich and Kuznetsova,[14] the active component of the vanadium–molybdenum oxide catalyst for the oxidation of acrolein to acrylic acid is the compound VMo_3O_{11}, whose maximum concentration in this system is reached at a V_2O_5 concentration of 7–15 mol%; the compounds VMo_2O_{8+x} and $V_6Mo_4O_{25}$ are also formed. Other additives are also frequently introduced into these systems. An effective additive to the vanadium–molybdenum catalyst for the synthesis of acrylic acid is copper oxide.[15] The introduction of the Cu ion gives a V–Mo–Cu oxide compound of variable composition, shown by X-ray diffraction, X-ray photoelectron spectroscopy, and infrared spectroscopy to be based on the structures of VMo_3O_{11} and VMo_2O_{3+x}.

The V_2O_5–MoO_3 system is an active catalyst for the oxidation of benzene to maleic anhydride. It contains the new compound $V_9Mo_8O_{40}$, and also V^{4+} ions, whose maximum concentration, according to EPR data,[16] corresponds to the limiting solubility of MoO_3 in V_2O_5 (about 30 mol%).

A vanadium–titanium oxide catalyst is used for oxidising *o*-xylene to phthalic anhydride.[17] The highest rate of formation of phthalic anhydride and the highest selectivity are observed when 2.5–8 mol% V_2O_5 is introduced into inactive titanium dioxide. Vanadium ions coordinated to titanium ions, and the compound V_6O_{13}, are formed in this system. EXAFS has shown[18] that titanium dioxide brings about disordering of the V_2O_5 structure.

Another example of the action of a modifier on the phase composition of a simple oxide catalyst is provided by the use of MoO_3 as additive. X-Ray diffraction and infrared and ultraviolet spectroscopy[19] have shown that when MoO_3 is introduced into inactive tin dioxide SnO_2 in the ratio Sn : Mo = 9 : 1, a solid solution of MoO_3 in SnO_2, and also Mo and Sn oxides, are detected in the system. This catalyst is used to oxidise propylene to acetone.

The rate of formation of acetone shows an extremal dependence on the concentration of Mo ions in SnO_2; the rate decreases when the Mo concentration is higher than that corresponding to the optimum ratio Sn : Mo = 9 : 1.

Thus the modification of simple oxides by various additives gives new catalytic systems consisting of solid solutions, new compounds, and microheterogeneous formations, with structures and phase compositions differing from those of the simple oxides.

2. Complex metal oxides

Multicomponent mixed oxide systems are highly effective catalysts for the selective oxidation of alkenes.

Bismuth and cobalt molybdates are most frequently used for the oxidation of propylene to acrolein. The vanadium–molybdenum oxide system is used to convert aromatic hydrocarbons into acid anhydrides, and vanadium–phosphorus catalysts are used to oxidise butane to maleic anhydride. The introduction of various additives into these systems increases their efficiency.

The addition of iron to bismuth molybdate gives a complex oxide system containing the triple oxide $Bi_2Fe_2Mo_2O_{12}$ and Bi and Fe molybdates. Table 1 gives data on the influence of the modification of the catalyst by iron on the rate and selectivity of the formation of acrolein from propylene.[20] The individual triple compound $Bi_2Fe_2Mo_2O_{12}$ has a low activity, and its catalytic properties are similar to those of bismuth molybdate. The modification of $CoMoO_4$ by Bi, Fe, and Sb additives leads to a sharp change in its catalytic properties in the oxidation of propylene to acrolein. The X-ray diffraction study of these systems[21] has shown that new compounds are formed (Table 2).

Table 1. Influence of the Fe ion on the activity and selectivity of the Bi–Mo catalyst.

Fe^{3+} concentration, at.%	Phase composition	Rate of formation of acrolein at 340 °C, ml m^{-2} min^{-1}	Selectivity with respect to acrolein, %
0	$Bi_2(MoO_4)_3$	0.44	88
2	$Bi_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, the triple compound $Bi_2Fe_2Mo_2O_{12}$	1.32	98
14.8	$Bi_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, the triple compound $Bi_2Fe_2Mo_2O_{12}$	3.75	91
33.3	the triple compound $Bi_2Fe_2Mo_2O_{12}$	0.58	87

Table 2. Modification of $CoMoO_4$.[21]

Composition of the catalyst	Phase composition
Co + Mo	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3
Co + Mo + Bi	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3, $Bi_2O_3 \cdot 3MoO_3$
Co + Mo + Bi + Fe	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3, $Fe_2(MoO_4)_3$, $Bi_2O_3 \cdot 3MoO_3$
Co + Mo + Bi + Fe + Sb	α-$CoMoO_4$, β-$CoMoO_4$, MoO_3, $Fe_2(MoO_4)_3$, $CoSb_2O_6$, $Bi_2O_3 \cdot 3MoO_3$

The catalytic system Co–Mo–Bi–Fe–Sb–O is used for the partial oxidation of isobutylene to methylacrolein. X-Ray diffraction and Mössbauer spectroscopy[22] have been used to study the structure of this multicomponent oxide system at different concentrations of the additives Bi and Fe. In addition to the basic matrix structure of $CoMoO_4$, the catalyst also contains the molybdates of bismuth $Bi_2(MoO_4)_3$ and iron(III) $Fe_2(MoO_4)_3$, and also the complex compound $M_2FeMo_2O_{12}$, where M = Bi, Sb. Figs. 3 and 4 give the dependence of the conversion of isobutylene and the relative concentration of the phases $Fe_2(MoO_4)_3$ and $M_3FeMo_2O_{12}$ on the concentrations of Bi and Fe in the system $Co_6Mo_{12}Bi_xFe_ySbO_z$. The maximum conversion of isobutylene is achieved for $x = 1$ and $y = 4-6$, when the catalyst contains equal quantities of the two iron-containing phases.

Thus the modification of complex oxide systems, which already contain several phases and elements in different oxidation states, leads to a further increase in their complexity. These complex oxide

systems make it possible to influence different stages of the oxidation and to increase the rate and selectivity of the reaction. The use of new complex catalytic systems has made it possible to achieve almost 90% selectivity, whereas on simple oxides the selectivity does not exceed 40–50%.

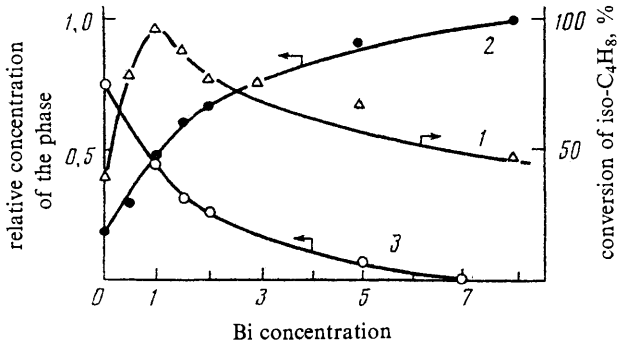


Figure 3. Dependence of the conversion of isobutylene at 370 °C (*1*) and the relative concentration of the phases $Bi_3FeMo_2O_{12}$ (*2*) and $Fe_2(MoO_4)_3$ (*3*) on the concentration of bismuth in the catalyst.[22]

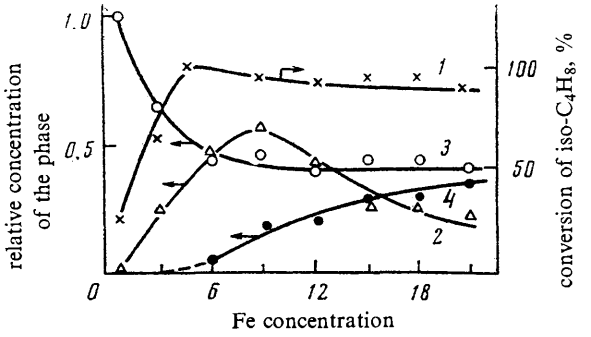


Figure 4. Dependence of the conversion of isobutylene at 370 °C (*1*) and the relative concentration of the phases $Fe_2(MoO_4)_3$ (*2*), $Bi_3FeMo_2O_{12}$ (*3*), and α-Fe_2O_3 (*4*) on the concentration of iron in the catalyst.[22]

III. The influence of additives on the state of oxygen in oxide catalysts

A large number of studies by different methods (using isotopes, reduction–reoxidation, etc.) have shown that the selective oxidation of organic substances on oxide systems involves the oxygen of the catalyst lattice.[5,23,24]

Oxidation involving the oxygen of the lattice is accompanied by the reduction of cations, which, when the process is carried out under stationary conditions, are reoxidised by the oxygen of the gas phase.

The formation of various non-stoichiometric oxides in the reduction of MoO_3 by the substance being oxidised has been examined.[24] The phase transitions do not involve extensive rearrangement of the lattice, but "crystallographic shearing" is observed,[25] that is during reduction, some of the oxygen is removed from the lattice with the production of vacancies, the distance between the Mo ions decreases, and the bonding between the oxygen octahedron around Mo is altered. The process gives blocks having a comparatively unaltered structure, separated by shear planes made up of other small blocks with a different regular structure.

In the reduction of MoO_3, the rapid movement of an electron into the bulk and its capture by Mo^{6+} ions close to a vacancy gives an Mo^{5+} ion

$$Mo_s^{6+}O_s + RH \rightarrow \left[\begin{array}{c} H \\ | \\ Mo_s^{5+}O_s \end{array}\right] R^+ \xrightarrow{Mo_v^{6+}O_v} Mo^{6+}\square\, RO + Mo_v^{5+}O_v + H^+.$$

The vacancy moves from the surface to the defect. The movement of the vacancy corresponds to the diffusion of oxygen to the surface by a mechanism involving a large number of displacements of the micro-blocks; thus the surface layer of the catalyst during the reaction is constantly rearranged, and the oxygen atoms change positions.

Table 3. Characteristics of the catalysts $Bi_{1-x/3}V_{1-x}Mo_xO_4$.[26]

x	Surface concentration of Bi, at.%	Rate of reduction by hydrogen $\times 10^{-6}$, mol min^{-1} m^{-2}	Mobility of the oxygen ions of the lattice,* %
0.00	20.6	12.1	37.0
0.09	14.6	8.7	57.4
0.21	15.1	7.8	75.1
0.27	14.6	7.6	72.2
0.45	14.0	6.4	100

*The fraction of oxygen ions of the lattice taking part in the oxidation, relative to the total quantity of oxygen ions of the lattice.

The introduction of additives into these systems influences the rate of migration of oxygen, and also the rate of rearrangement of the oxide lattice. The rates of these processes depend on the mobility of the oxygen of the solid lattice. The composition dependence of the mobility of oxygen in the $Bi_{1-x/3}V_{1-x}Mo_xO_4$ system, used to oxidise propylene to acrolein, has been studied using ^{18}O.[26] Table 3 gives the rates of the reduction by hydrogen of catalysts with different compositions, and data characterising the mobility of the lattice oxygen. The rate of reduction by hydrogen changes in the opposite sense to the change in the rate of reduction by propylene, that is the ability of the catalysts to undergo reduction is influenced strongly by the nature of the reducing agent. The dependence of the rate of reduction on the nature of the reducing agent is apparently due to the fact that the reactions of different reagents with the oxygen of the catalyst take place on different active centres. Increase in the concentration of the additive in the catalyst alters the composition of the surface, influencing the rate of its reduction and the activity.

A microcatalytic method combined with Mössbauer spectroscopy has given quantitative data on the reduction by propylene of cobalt molybdate modified by added Fe and Bi.[27] Fig. 5 gives the Mössbauer spectra (MS) of iron in the original Co–Mo–Bi–Fe oxide catalyst and in the catalyst reduced at different temperatures. In the oxidised state, Fe is present in crystalline $Fe_2(MoO_4)_3$, and the chemical shift is $\delta E_I = 0.68 \pm 0.01$ mm s^{-1}. When this catalyst is treated with propylene, partial reduction takes place to give β-$FeMoO_4$. Fig. 5 shows that the extent of the reduction, determined from the ratio of the areas of the spectra as $[Fe^{2+}]/([Fe^{2+}] + [Fe^{3+}])$, increases sharply with temperature; it has the values 0.14 at 270 °C, 0.44 at 350 °C, and 0.76 at 390 °C. These spectroscopic data were used to calculate the quantity of oxygen removed from the lattice in the reduction of $Fe_2(MoO_4)_3$ to $FeMoO_4$. The results of this calculation are compared with the data obtained in the catalytic micro-reactor in Table 4.

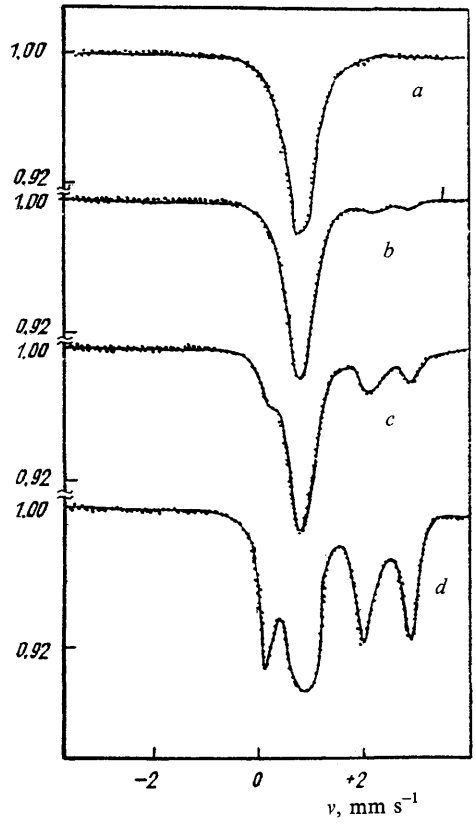


Figure 5. Mössbauer spectra of a Co–Mo–Bi–Fe catalyst before (*a*) and after its reduction by propylene at 270 (*b*), 350 (*c*), and 390 °C (*d*).[27]

Table 4 shows that almost all the oxygen removed belongs to iron molybdate. The Mössbauer spectrum of the reoxidised catalyst is identical to the original spectrum.

The liberation of the oxygen of iron(III)molybdate to give divalent iron molybdate and anion vacancies takes place according to the scheme:

$$Fe_2(MoO_4)_3 \rightarrow \{2FeMoO_4(MoO_3)\}\,\square_x + x[O],$$

where □ represents an anion vacancy.

The ionisation of vacancies leads to the production of an excess negative charge;[28] a redistribution of electron density takes place, affecting the entire iron molybdate crystal and leading to its reduction. Thus the modification of the Co–Mo catalyst leads to the formation of iron molybdate which "supplies" the oxygen for the selective oxidation of hydrocarbons.

Table 4. Quantity of oxygen (*n*) removed from a Co–Mo–Bi–Fe catalyst by the reaction with 40 C_3H_6 pulses.[27]

Reduction temperature, °C	10^{-19} *n*, atom g^{-1}	
	kinetic data	Mössbauer data
270	2.2	2.5
350	7.0	8.0
390	11.0	13.0

The removal of oxygen from the catalyst lattice under the influence of a hydrocarbon is accompanied by a simultaneous change in the oxidation state of the metal ions; if two additives are introduced into the catalyst, charge transfer takes place between them.

Mössbauer spectroscopy has been used to study the reactions of Fe and Te, introduced into $CoMoO_4$, with the components of the reaction mixture during the oxidation of propylene to acrolein.[29] On modification, the activity of the catalyst and the selectivity of the oxidation increase several-fold (Table 5). Spectroscopic data show that the introduction of the additives into the oxide catalyst gives new compounds $Fe_2(MoO_4)_3$ and $CoTeO_4$; reaction with the mixture leads to a partial change in the oxidation states of the Fe and Te ions.

Table 5. Influence of added Fe and Te on the activity of $CoMoO_4$ and the electronic transitions.[29]

Additive	Change in oxidation number	Conversion of C_3H_6, %	Selectivity of C_3H_4O formation, %
None	—	10	10
Fe	$Fe^{3+} \rightarrow Fe^{2+}$	63	36
Te	$Te^{6+} \rightarrow Te^{4+}$	55	30
Fe + Te	$Te^{6+} \rightarrow Te^{4+}$ $Fe^{3+} \rightarrow Fe^{2+}$	72	44

The rate of oxidation of different organic substances on V_2O_5, V_2O_5–MoO_3, and other vanadium-containing catalysts is generally proportional to the concentration of V^{4+}, which is formed during

the process as a result of redox reactions, and also under the influence of the additive. The change in the oxidation state of vanadium is accompanied by the formation of a $V^{4+}=O$ double bond; this form of oxygen is more active in selective oxidation than other forms.

The influence of added P, Mo, W, and Sn on the catalytic properties of V_2O_5 in the oxidation of benzene to maleic anhydride has been studied.[30–32] Mo ions increase the activity of the catalyst and the selectivity of the process, whereas W and P increase the selectivity but decrease the activity. The presence of Sn ions in V_2O_5 leads to the extensive oxidation of benzene. This influence of the additives on the catalytic properties was related to their electronegativities:

$$Sn^{4+} < V^{5+} < W^{6+} < P^{5+} < Mo^{6+}.$$

The introduction of the more electronegative ions (W, P, Mo) leads to a decrease in the electron density of the $V^{4+}=O$ bond, associated with charge transfer between the vanadium ions and the additive, leading to a change in the length of the $V^{4+}=O$ bond. When this bond becomes shorter, the oxygen becomes more reactive, and the catalyst becomes more effective in the oxidation of benzene.

Thus the state and reactivity of oxygen are related to the structure of the catalyst and the electron transitions in the solid. The rearrangement of the structure and the change in the rate of electron transfer under the influence of the additives are factors determining the selectivity of oxidation processes and the activity of catalysts.[28]

IV. The modification of catalysts by acidic and alkaline additives

1. Oxide systems

There is a large amount of data (see for example the published review[33]) on the action of alkaline additives in catalysts on various reactions. The trivial explanation of this phenomenon reduces to the examination of the acid–base properties of the surface of the solids and the reagents. The alkaline and acidic properties of the reaction products and the strength of their bonding with the surface[34] are regarded as factors determining the activity of the catalysts.

It has been shown for the case of the vanadium–molybdenum oxide system that the selectivity of the oxidation of benzene to maleic anhydride can be increased by introducing both alkaline (Na) and acidic (P) additives into the catalyst.[34] This increase in selectivity is probably due not to a change in the acid–base properties of the catalyst but to some other factors. EPR has shown that the presence of Na and P in the catalyst leads to an increase in the concentration of V^{4+} ions and the number of V=O bonds, and XPS has shown a change in the ratio of the ions $Mo^{6+}:V^{4+}$ in the layers next to the surface.

When the ions Na, K, Rb, and Cs were introduced into the vanadium–titanium catalyst for oxidising *o*-xylene to phthalic anhydride (PA),[35] the selectivity of the process increased and reached 87%, as a result of a decrease in the rate of the more extensive oxidation of PA. The selectivity of the formation of PA increases with increase in the electronegativity of the alkali metal ions. All the alkaline elements added to the catalyst keep the vanadium in the vanadium–titanium oxide catalyst in the stable oxidation state, and simultaneously neutralise the acidic centres of the surface.

The introduction of the K ion into the Sn–Mo–Fe catalyst for the oxidation of propylene to acetone increases the selectivity from 23% to 94% by decreasing the rate of more extensive oxidation. The presence of the K ion leads to an increase in the concentration of the reduced form of Mo produced by reaction with propylene.

The influence of alkali metals (Li, Na, K) and alkaline earth metals (Mg, Ca, Ba) on the properties of the unique vanadium–phosphorus catalyst for the oxidation of butane to maleic anhydride has been studied.[36] No relationship between the acidic properties of the surface and the rate of oxidation of butane was detected, but a change in the bond energy of oxygen in the lattice and in the catalytic properties on modification was observed.

The mechanism of the action of alkaline additives has been studied in more detail for the Co–Mo–Bi–Fe catalyst for the partial oxidation of alkenes to unsaturated aldehydes. When the catalyst is modified by Li, Na, K, and Cs, the acid–base properties of its surface remain unchanged.[37] At the same time, modern physical methods (Mössbauer spectroscopy, EPR, ESCA) have shown that the alkali metals influence the structure of the catalyst. The modified Co–Mo–Bi–Fe catalyst contains the phase $Fe_2(MoO_4)_3$ with a garnet-like structure, which includes an unoccupied dodecahedral sub-lattice. On the introduction of the alkali metals, in particular potassium, whose ionic radius is the optimum for this structure, partial filling of the unoccupied sub-lattice takes place; defects are produced in $Fe_2(MoO_4)_3$, which acquires the structure of a non-stoichiometric garnet containing oxygen vacancies:

$$\square_3^0 Fe_2^{3+}(Mo^{6+}O_4^{2-})_3 \xrightarrow{K^+} K_x^+ \square_x^- \square_{3-x}^0 Fe_2^{3+}(Mo^{6+}O_4^{2-})_3,$$

where $\square^0$ represents a vacancy in the dodecahedral sub-lattice, and $\square^-$ represents an oxygen anion vacancy.

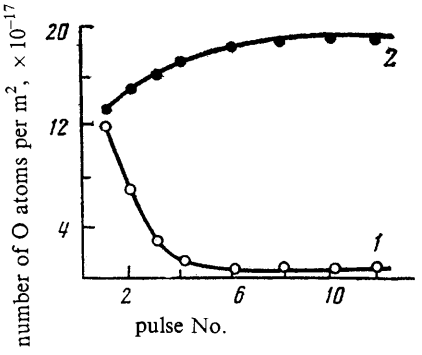


Figure 6. Dependence of the quantity of oxygen of the lattice of the catalysts Co–Mo–Bi–Fe (*1*) and Co–Mo–Bi–Fe–K (*2*) reacting with iso-C_4H_8 in each separate pulse on the number of successive pulses.[38]

These structural changes also have a marked influence on the mobility of the oxygen of the catalyst lattice. Modification of the Co–Mo–Bi–Fe catalyst by potassium leads to an increase in the conversion and the selectivity of the oxidation of isobutylene to methylacrolein. To establish the influence of modification on the

mobility of oxygen of the catalyst, its reduction by isobutylene was studied by the kinetic method and by Mössbauer spectroscopy.[38] Fig. 6 shows the change in the quantity of oxygen reacting in each pulse with isobutylene (size of the pulse 2 ml) in a catalyst with and without the addition of potassium. The concentration of isobutylene on the modified catalyst in each subsequent pulse does not decrease, but increases, and becomes constant after 8–10 pulses. The decrease in the conversion becomes significant only after 25–30 pulses.

The rate of reduction of the catalyst also increases after its modification by potassium. This can be seen particularly clearly after the supply of the fourth or fifth pulse of iso-C_4H_8; at this moment the rate of reduction of the Co–Mo–Bi–Fe catalyst decreases to almost one tenth of the initial rate, and the rate of reduction of Co–Mo–Bi–Fe–K even increases slightly (Table 6). The extent of the reduction of the modified catalyst, that is the quantity of oxygen removed in the reaction with a given number of alkene pulses, is almost ten times greater than that on the catalyst without K.

Table 6. Rate (v_r) and extent (n_0) of the reduction of catalysts by isobutylene.[38]

Catalyst	Conversion of iso-C_4H_8, %	Selectivity of C_4H_6O formation, %	n_0 (atom m^{-2}) after 10 pulses	v_r, μmol m^{-2} s^{-1}	
				initial	after 5 pulses
Co–Mo–Bi–Fe	57	40	$27 \cdot 10^{17}$	0.63	0.05
Co–Mo–Bi–Fe–K	76	83	$18 \cdot 10^{18}$	0.70	0.80

Analysis of the Mössbauer spectra and comparison with the kinetic data obtained in a microcatalytic reactor showed that the reduction of the catalyst involves mainly the oxygen of the $Fe_2(MoO_4)_3$ lattice. When the K ion is introduced into the catalytic system, it is the mobility of the oxygen in this lattice that is increased, as indicated by the spectra of the reduced specimens; in the Co–Mo–Bi–Fe specimen, the extent of the reduction, calculated from the ratio of the normalised areas in the spectrum of Fe^{2+} molybdate to the total area of the spectrum of Fe^{2+} and Fe^{3+} molybdates, is 0.12, whereas that in the Co–Mo–Bi–Fe–K specimen is 0.75.

Modification of the Co–Mo–Bi–Fe catalyst by acidic additives (for example P) leads to a marked deterioration in its catalytic properties.[27] The conversion of C_3H_6 decreases from 87% to 14%, and the selectivity of the oxidation to acrolein decreases from 60% to 32%. The introduction of phosphorus, like that of potassium, produces practically no change in the acid–base properties of the catalyst surface. X-Ray diffraction and Mössbauer spectroscopy have shown that the presence of phosphorus prevents the formation of crystalline iron(III)molybdate in the catalyst. The rate and extent of the reduction of the Co–Mo–Bi–Fe–P catalyst by propylene are ten times lower than those for Co–Mo–Bi–Fe.

Thus the change in the catalytic characteristics of oxide systems under the influence of alkaline and acidic additives is not always due to their influence on the acid–base properties of the catalyst surface.[39] As shown above, these additives influence mainly the structure of the solid and the mobility of the reactive oxygen, leading to a change in the selectivity of the oxidation processes.

2. Silver catalyst

Only the metallic catalyst silver is used for the partial oxidation of ethylene to ethylene oxide. This process has been the subject of a large number of studies[5,6,8] to determine the mechanism of formation of C_2H_4O, the nature of the surface of the catalyst, the state of oxygen, etc. Modification by alkaline and acidic additives (K, Cs, Cl, etc.) is widely used to produce an active and selective silver catalyst.

To determine the mechanism of the action of the additives, it is necessary to examine the forms of oxygen adsorbed on silver, taking part in the oxidation of ethylene.

The following scheme has been given[40] for the reaction of oxygen with silver:

1. $O_2 + Ag \rightarrow O^-_{2\,ads} + Ag^+$,
2. $O_2 + 4Ag(\text{individual atoms}) \rightarrow 2O^{2-}_{ads} + 4Ag^+$,
3. $O_2 + 4Ag(\text{aggregate of atoms}) \rightarrow 2O^-_{ads} + 4Ag(\text{aggregate})$.

Other authors[41,42] consider that isolated silver atoms adsorb oxygen in the molecular form, which then takes part in the oxidation of C_2H_4 to C_2H_4O. Carbon dioxide is formed by the reaction between C_2H_4 and atomic oxygen, which is adsorbed on the aggregate (4Ag). A different view is held by other workers,[43] who consider that the formation of C_2H_4O also involves atomic oxygen. In addition to the production of surface forms, the adsorption of oxygen on polycrystalline silver is accompanied by its solution in the layers of the metal lattice next to the surface.[44]

In the opinion of other workers,[45] dissolved oxygen weakens the bonds between the surface forms of oxygen and the catalyst. The study by modern spectroscopic methods of the action of alkali metal ions adsorbed on different faces of silver showed that these additives increase the rate of the recombination of atomic oxygen to molecular oxygen, and hence increase the degree of covering of the surface by molecular oxygen. Thus on the (111) face of silver on which caesium ions were adsorbed, an oxygen-containing surface structure was detected.[46,47] The addition of caesium decreases the rate of the extensive oxidation of ethylene and alters the activation energy of formation of CO.

Modification of silver by caesium ions changes not only the concentration of oxygen on the surface but also the rate of isomerisation of C_2H_4O.[48]

When the Rb^+ ion is added to silver, the formation of peroxide leads to the production of molecular oxygen by the reaction

$$2\,Rb_2O_4 \rightarrow 2\,Rb_2O + 3\,O_2,$$
$$2\,Rb_2O \rightarrow 4\,Rb + O_2$$

The introduction of the K^+ ion into Ag (110 face) also alters the degree of covering of the surface by oxygen; K_2O_4 is formed, and decomposes by a scheme similar to that for rubidium peroxide.[50]

The addition of alkali ions to silver alters the ratio of the rates of formation of C_2H_4O and CO_2 in the oxidation of ethylene, and also the activation energies of these reactions, so that it influences the selectivity of the process.

The introduction of the Cl ion into a single crystal of Ag (111 face) leads to the displacement of the previously adsorbed oxygen atom.[51] Changes are observed in the rate and order of the

reaction and in the activation energy for the formation of ethylene oxide and CO_2, depending on the degree of covering of the surface by chlorine (Fig. 7). According to other data,[52] chloride ions adsorbed on silver form a surface structure of silver chloride AgCl. The adsorption of Cl ions increases the diffusion of oxygen atoms into the silver lattice.[53]

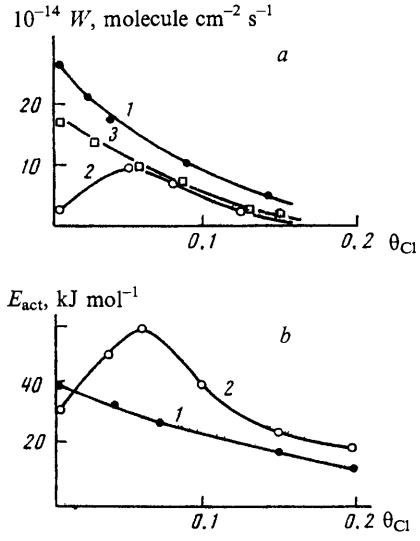


Figure 7. Effect of the degree of covering of the silver surface with chlorine on the rate (*a*) and activation energy (*b*) of formation of ethylene oxide and CO_2:[51] *1*, carbon dioxide; *2*, ethylene oxide; *3*, total rate of transformation of ethylene.

Silver is often modified by chlorine by introducing dichloroethane into the reaction mixture. This method of introducing additives has been called "gas modification",[2] and its mechanism is the same as the usual mechanism of action of additives introduced into a catalyst. On the silver surface, dichloroethane dissociates to form AgCl.[5] Experiments using the ^{36}Cl isotope have shown that the silver chloride formed in the reaction medium is reduced with the generation of a Cl ion, which does not migrate into the metal lattice at 330 °C, but remains on the surface. Similar results were obtained using the ^{131}I isotope.

In the modification of silver, dichloroethane undergoes the following transformations:

$$C_2H_4Cl_2 + Ag \rightarrow Ag(C_2H_4Cl_2)_{ads} \xrightarrow{O_2} \overbrace{Ag\,[AgCl]}^{Ag+(Cl^-)_{ads}} + C_2H_4.$$

Dichloroethane added to the $C_2H_4 + O_2$ reaction mixture inhibits the dissociation of oxygen on silver.[54] The concentration of the modifying additive appears in the kinetic equation for the reaction.

Thus when the potassium ion is introduced into the silver catalyst:

1, the chemisorption of oxygen is increased,

2, peroxides generating molecular oxygen are formed,

3, the rate of recombination of oxygen atoms increases,

4, the rate of isomerisation of ethylene oxide changes,

5, the kinetic parameters of the oxidation of ethylene change.

When the chloride ion is added:

1, the rate of dissociation of molecular oxygen decreases,

2, the strength of the Ag–O bond decreases,

3, the rates of desorption and recombination of oxygen atoms and their diffusion into the Ag lattice increase,

4, chloride ions displace oxygen atoms from the silver surface,

5, the kinetic parameters of the oxidation of ethylene are altered.

Modification of silver influences not only the state of the adsorbed oxygen but also the adsorption of C_2H_4. Ethylene is adsorbed on the silver surface only in the presence of oxygen, reacting with it to form surface complexes whose structure has been studied by infrared spectroscopy.[55] It was previously shown that on adsorption, ethylene is positively charged, but the work function depends on the magnitude of the negative charge on oxygen. The presence of the Ag surface of additives with positive (alkali metals) or negative (halogens) charges alters the heats of adsorption and the bond energies of oxygen and ethylene–oxygen complexes with the surface. This electronic factor should probably also influence the activation energies of the partial and extensive oxidation of ethylene. A study of the combined adsorption of potassium and chlorine on the (100) face of a single crystal of Ag showed that an electrostatic interaction takes place between the Cl^- and K^+ ions.[56] AgCl, stabilised by K^+ ions, is formed on the surface. In addition, KCl, desorbed at 700 K, was also detected.

Thus as in oxide systems, the introduction of acidic and alkaline additives into silver influences chiefly not the acid–base properties of the surface but the forms in which oxygen is adsorbed on the metal, and also the kinetics of the oxidation of ethylene to ethylene oxide.

V. Summary

The term modification is now used to describe not only the introduction of additives into different catalysts but also the change in the quality of the surface, for example the replacement of OH groups in silica gel by various elements, the deposition of various complexes and molecules on the surface, etc.

It is assumed[57] that the modification of simple and complex catalytic systems involves a change in the structure of the solid or a reconstruction of its surface, and also a change in the energy of the bonds between the adsorbed reagents and the surface. It has been noted that modified systems are multi-functional, and that the selectivity can be controlled by controlling their structure.

Attention was drawn above to the fact that practically all selective oxidation catalysts are multi-phase (even in the case of solid solutions, for example $Sb_2O_4-SnO_2$).

Modern spectroscopic methods have detected the migration of the additive from the bulk to the surface with the formation of a separate phase in both oxide and metallic catalysts. When silver is modified by alkali and halide additives, new compounds, peroxides and salts, are produced on the surface.

Since modified catalysts are multi-phase, a separation of functions between different phases has been suggested.[58,59] An example is provided by the oxidation of propylene on a cobalt–molybdenum oxide catalyst modified by Bi and Fe, which consists of Co, Bi, and Fe molybdates. During the oxidation of propylene under stationary conditions, partial reduction of the molybdate $Fe_2(MoO_4)_3$ to $FeMoO_4$ takes place, with the production at the interface between these phases of a super-equilibrium concentration of vacanices, which, by diffusing to the $Fe_2(MoO_4)_3/\beta$-$FeMoO_4$ interface, can act as centres for the dissociative adsorption of oxygen from the gas

phase with the formation of lattice oxygen. The transfer of this oxygen to the active regions of the surface, on which the alkene is adsorbed and oxidised, takes place via the interface between the iron and bismuth molybdate phases. A possible model of a system of this kind is shown in Fig. 8. The phase transitions $Fe_2(MoO_4)_3 \rightleftarrows FeMoO_4$ are facilitated if the catalytic system contains the isostructural phase β-$CoMoO_4$, since the interphase boundaries of β-$FeMoO_4$ and β-$CoMoO_4$ are coherent, and the formation of $FeMoO_4$ in the presence of a sufficient quantity of anion vacancies is associated with practically no energy barrier.

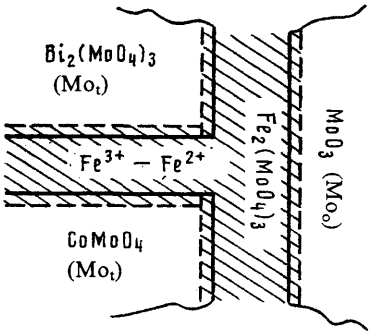


Figure 8. Model of the boundary zone of a Co–Mo–Bi–Fe–O catalyst;[60] Mo_o and Mo_t correspond to octahedral and tetrahedral coordination of the molybdenum ion.

The quantity of anion and cation defects depends on the total extent of the interface between the crystallites of the different phases in the catalyst, and this extent in turn is determined by the size of the actual crystallites, that is by their degree of dispersion. The degree of dispersion of multi-phase and multi-component oxide catalysts based on the molybdates of various divalent metals depends on their composition.[60]

A study of the oxidation of propylene to acrolein on complex oxide catalysts with the general formula $M^{II}_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$, where M^{II} = Co, Mg, Zn, Mn, established that the highest catalytic activity is shown by the systems with M^{II} = Co and Mg.[60] The Co and Mg molybdates in these systems, like the other phases, are characterised by the maximum degree of dispersion. For M^{II} = Zn and Mn, the individual crystallites are much larger, and the activity of these catalysts is much lower. At the same time, it was shown that the chemical nature of the cation M^{II} in this complex catalyst has practically no influence on the overall activity; in this case the catalytic properties are influenced significantly by the degree of dispersion. The additives introduced into complex oxide catalysts can be divided into two types: those of one type take direct part in the functioning of the active centre and facilitate some stage of the process (for example Fe ions in the Co–Mo–Bi–Fe catalyst), while those of the other type create a definite "macro-structure" (for example Co and Mg ions in the M^{II}–Mo–Bi–Fe system). The action of additives of the first type is called "micro-modification", and that of the second type "macro-modification".[60]

The effect of modification is revealed particularly clearly in the action of the alkali metals on a catalyst. These additives are capable of producing new basic centres on the surface. In addition, the alkali metals can form new compounds (for example salts, bronzes in the case of vanadium catalysts, etc.) and hence increase the multi-phase character of the catalytic system. The alkali metals may also be introduced into the structure, facilitating its rearrangement (for example, when the K^+ ion is introduced into iron molybdate with the garnet structure, it acquires a non-stoichiometric structure with a larger number of defects). All these changes influence the state of oxygen in the catalytic systems. It is believed[61] that the modification by alkali metals of oxide catalysts for the oxidation of hydrocarbons alters the ratio of nucleophilic and electrophilic oxygen on the surface. It is suggested that these forms are involved in the oxidation. To achieve a high selectivity of partial oxidation, it is necessary to suppress extensive oxidation. Both processes involve molecular and atomic oxygen and the oxygen of the oxide lattice. Additives control the concentrations of these forms of oxygen on the oxide surface, and hence alter the ratio of the products of mild and extensive oxidation.

In the present review, most attention has been paid to the promoting action of additives and its mechanism. Increase in the concentration of additives in a catalyst beyond a certain limit, however, decreases the reaction rate and alters the activation energy. The mechanism of this "poisoning" is less clear, and has been little studied. Increase in the concentration of additive probably leads to an increase in the concentration in the system of new compounds which in a number of cases are inactive and decrease the number of active centres. For example, with increase in the concentration of iron ions in the Co–Mo–Bi–Fe system, the products include not only iron molybdate but also iron oxide, on which propylene undergoes extensive oxidation, so that the selectivity of the formation of acrolein from the alkene decreases sharply. This phenomenon is particularly characteristic of solid solutions, in which increase in the quantity of additive exceeds the solubility limit, and an inactive oxide phase separates. In addition, the active centres of the catalyst may be blocked by additive ions, as observed on a silver catalyst with increase in the concentration of Cl^- ions.

The decrease in activity with increase in the concentration of an additive may also be due to a phase transition in one of the compounds in the catalyst. For example, increase in the vanadium concentration in the V_2O_5–TiO_2 system leads to a phase transition in TiO_2 from the rutile to the anatase structure,[62] and the catalyst is deactivated.

The decrease in the catalytic activity of modified catalysts may also be due to reaction between the reaction medium and the solid. The optimum concentration of additives ensuring the maximum activity of a catalyst can be lost by the partial removal of the elements of these additives by the reaction mixture. This takes place, for example, with the phosphorus ion in a V–Ti–P oxide catalyst[62] or with the Cl ion in a silver catalyst.[5] Decrease in the concentration of the additive lowers the activity of the catalyst, and mimics its "poisoning".

In catalytic oxidation, electronic interaction takes place between the ions in the catalyst. At the optimum concentration of the additive, these transitions are facilitated, since a new lattice structure facilitating the transport of electrons is produced. If the concentration of additive exceeds the optimum value, breakdown of the relative arrangement of these ions and the production of electron traps become possible. In this case there is also a decrease in the rate of individual reactions, and "poisoning" of the catalyst takes place.

Thus the modification of various catalytic systems involves the formation of new compounds in the bulk and on the surface of the catalysts, and changes the number and composition of the active

centres, the structure of the solid, its ability to undergo rearrangement, and the electronic interactions between the elements in the catalyst. Additives influence the kinetics (reaction rate, activation energy) and mechanism (structure of surface compounds, energies of their bonds with the surface) of a reaction.

It is difficult to predict the action of different additives, since they influence many functions of catalysts. Modification, however, makes it possible to produce effective catalysts for the oxidation of various organic compounds.

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Cement-containing catalysts

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ABSTRACT. The most important achievements in the development and use of cement-containing catalysts for a number of organic and inorganic processes have been reviewed. The possibilities for development in this branch of catalysis have been discussed.

The bibliography contains 365 references.

Contents

I.	Introduction	450
II.	The mechanism of formation of cement-containing contact catalysts	450
III.	Carriers and adsorbents based on cements	451
IV.	The production of metal-cement catalysts	453
V.	Catalysts for the methanation of oxides of carbon	454
VI.	Catalysts for the conversion of hydrocarbons	455
VII.	Catalysts for obtaining protective atmospheres	456
VIII.	Catalysts for purifying sulphur-containing gases	457
IX.	Catalytic systems for the conversion of CO by water vapour and the synthesis and decomposition of methanol	457
X.	Catalysts for the hydrogenation of oxygen	459
XI.	Catalysts of the Fischer–Tropsch synthesis	459
XII.	Cement-containing contact catalysts with an acid–base action	459
XIII.	Catalytic systems for various organic and inorganic processes	460

I. Introduction

Industry is making increasing demands in relation to the activity, selectivity, operational lifetime, mechanical strength, and durability of catalysts. A new direction in the solution of these problems is being opened up by the inclusion of aluminates of calcium (AC) and cements in catalytic compositions. These catalysts are used in the transformation of hydrocarbons, the conversion of methane and naphtha, the purification of gases from oxides of carbon, the dissociation of ammonia, sulphur purification, the conversion of carbon monoxide, the production of glycerol, etc.[1–8] Various aspects of the use of cements for these purposes may be noted.

1. One of the features of cements favouring their use in catalysis is their high mechanical strength. 2. The efficiency of both low-temperature and high-temperature processes depends on the thermal stability of heterogeneous catalysts, and heat resistance is an inherent property of alumina cement.[9] 3. The stability of catalysts used in the treatment of hydrocarbon raw material is determined to a large extent by their stability to coke formation. The cost of combating coke formation sometimes exceeds the cost of the actual catalytic processes.[10] One method of eliminating or preventing coke formation is by introducing basic additives, in particular as cements. 4. The large-scale production of cements, combined with the restricted supply of raw materials for the production of carriers (Al_2O_3, MgO, SiO_2, etc.), has provided a convincing reason for using various cements, in particular high-alumina cements, for this purpose. 5. The important role of the carrier in the production of heterogeneous contact catalysts[11] makes it necessary to study the texture of calcium aluminate sorbents and to develop carriers with a highly developed and controllable surface.[12] 6. Finally, the use of cements in catalysts is encouraged by the efforts to combine a high activity of catalytic systems with ecological cleanliness and waste-free methods of production.

II. The mechanism of formation of cement-containing contact catalysts

In the late sixties and early seventies, the study of the mechanism of formation of nickel-cement (nickel–aluminium–calcium) catalysts obtained by chemical mixing,[7,8,13,14] led to the discovery of the reaction of the cements (calcium aluminates) with the source of the active component (the nickel salts) in the aqueous medium. The reaction takes place at room temperature, and is accompanied by marked changes in texture and phase composition. This made it necessary to re-examine the view that the calcium aluminates and cements were merely hydraulic binding agents.

It was subsequently shown that the mechanism of the reaction of basic metal carbonates with calcium aluminate cements is the same for nickel,[7,8,13–23] zinc,[17,19–26] copper,[17,19–23,27] cobalt,[19–23] copper–zinc,[28] cobalt–manganese,[29] and cobalt–copper[30] contact catalysts. Metal hydroxide carbonates (MHC) react with calcium aluminates in aqueous or aqueous–ammoniacal media to give a multi-phase system. The composition of the reaction products indicates both hydration of the cements and an exchange reaction between the calcium aluminates and the metal hydroxide carbonates. Depending on the conditions, the reaction gives the metal hydroxoaluminates, $CaCO_3$, $Al(OH)_3$, $M(OH)_2$, $Ca_3[Al(OH)_6]_2$, and $Ca(OH)_2$. The metal hydroxoaluminates (MHA) have the following characteristics: a, their structure contains water as OH groups; b, the ratio M/Al in them is close to 1.5, particularly in an aqueous medium, but not in an aqueous–ammoniacal medium, in which some of the metal is lost as ammines; c, they can be synthesised from salts, which act as the source of the metal and aluminium, the latter being present as the $Al(OH)_4^-$ anion; d, on thermal decomposition they give MO and MAl_2O_4, so that in the original MHA the molar ratio $MO/Al_2O_3 > 1$; e, many metal hydroxoaluminates have the formula $M_3Al_2(OH)_{12}$. Since calcium hydroxoaluminates on dissolving in water give Ca^{2+} and $Al(OH)_4^-$, the reaction of MHC with alumina cements can be represented as follows: Ca^{2+} ions react with CO_3^{2-} ions in the labile structure of the MHC to give sparingly soluble $CaCO_3$, whose formation displaces the reaction to the right. To preserve the electrical neutrality of the MHC, the place

of one CO_3^{2-} ion carrying two negative charges must be taken by two $Al(OH)_4^-$ ions, each of which carries only one negative charge:

$$a\,[m\,MCO_3 \cdot n\,M(OH)_2] + 3\,Ca^{2+} + 2\,Al(OH)_4^- + 4\,OH^- = \\ = M_3Al_2(OH)_{12} + (3 - am)\,Ca(OH)_2 + (an + am - 3)\,M(OH)_2 + \\ + am\,CaCO_3, \quad (1)$$

$m \leqslant n$; $m = 1, 2$; $n = 1, 2, 3$

Since $M_3Al_2(OH)_{12}$ has a layer crystal lattice, insertion of $M(OH)_2$ into it is possible, so that the ratio M/Al will increase. In addition to metal hydroxoaluminates, hydroxocarbonatoaluminates may also be formed:

$$a\,[m\,MCO_3 \cdot n\,M(OH)_2] + 3Ca^{2+} + 2\,Al(OH)_4^- + 4\,OH^- = \\ = M_3Al_2(OH)_8(CO_3)_2 + (5 - am)\,Ca(OH)_2 + \\ (an + am - 3)\,M(OH)_2 + (am - 2)\,CaCO_3. \quad (2)$$

The reactions of MHC with calcium mono- and dialuminates are described by the equations

$$3\,CaAl_2O_4 + 12\,H_2O + a\,[m\,MCO_3 \cdot n\,M(OH)_2] = \\ = am\,CaCO_3 + \left(\frac{3 - am}{3}\right) Ca_3[Al(OH)_6]_2 + \\ + \left(\frac{an + am}{3}\right) M_3Al_2(OH)_{12} + \left(\frac{12 - 2an}{3}\right) Al(OH)_3, \quad (3)$$

$$3\,CaAl_4O_7 + 21\,H_2O + a\,[m\,MCO_3 \cdot n\,M(OH)_2] = \\ = \left(\frac{an + am}{3}\right) M_3Al_2(OH)_{12} + am\,CaCO_3 + \\ + \left(\frac{3 - am}{3}\right) Ca_3[Al(OH)_6]_2 + \left(\frac{30 - 2an}{3}\right) Al(OH)_3 \quad (4)$$

In an aqueous–ammoniacal solution, part of the MHC is converted into a carbonatoammine complex. The composition of the reaction products and the extent of the reaction depend on the numerical values of the coefficients *a*, *m*, and *n* (if M = Ni or Co, *m* = 2 and *n* = 3; if M = Zn, *m* = 1 or 2 and *n* = 3; if M = Cu, *m* = *n* = 1). The reactions according to Eqns. (1)–(4) are determined by the ratio of *a* to the values of *m* and *n*. With increase in *a*, the yield of $CaCO_3$ and $M(OH)_2$ increases, and the proportion of $Ca(OH)_2$ decreases. At certain ratios, the reaction will take place according to different stoichiometric equations. Thus when M = Ni, Cu, Zn, or Co, $M(OH)_2$ must take part in the reaction at low values of *a*, and $Ca(OH)_2$ must take part at high values of *a*. The range of possible values of *a* in the case of the formation of hydroxocarbonatoaluminates [Eqn.(2)] is broader than for the formation of MHA. The phase composition of cement-containing catalysts is described extremely accurately by general equations based on the reaction between metal hydroxide carbonates and $CaAl_2O_4$ ($CaAl_4O_7$). The thermal decomposition of the compounds formed by the chemical reaction and containing the active component can be described by the equations

$$M_3Al_2(OH)_{12} \xrightarrow[-H_2O]{} 3MO.Al_2O_3 \text{ (solid solution)} \rightarrow 2MO + MAl_2O_4, \quad (5)$$

$$M_3Al_2(OH)_8(CO_3)_2 \xrightarrow[-H_2O,\ CO_2]{} 3MeO.Al_2O_3 \text{ (solid solution)} \\ \rightarrow 2MO + MAl_2O_4. \quad (6)$$

If two metal hydroxide carbonates take part in the reaction simultaneously (Cu and Zn, Co and Cu, Ni and Cu), the first stage of the reaction gives mixed hydroxide carbonates, from which are formed mixed hydroxoaluminates (possibly hydroxocarbonatoaluminates), which are readily converted into mixed solid solutions

$$m'M'CO_3.n'M'(OH)_2 + m''M''CO_3.n''M''(OH)_2 + CaAl_2O_4(CaAl_4O_7) \\ + H_2O \rightarrow M'M''Al_2(OH)_{12} \\ \rightarrow M'O.M''O.Al_2O_3 \text{ (solid solution)}. \quad (7)$$

Solid solutions of mixed metal hydroxoaluminates and hydroxocarbonatoaluminates are formed from the anion-modified oxides (anionic group OH^- or CO_3^{2-}),[11] that is the oxides of Al, Cu, Co, Ni, Zn; naturally, the solid solutions obtained are also anion-modified.

The reaction of metal hydroxide carbonates with Ca^{2+} and $Al(OH)_4^-$ ions, represented by Eqn. (1) above, can be represented differently:

$$m\,MCO_3 \cdot n\,M(OH)_2 + m\,Ca^{2+} + 2m\,Al(OH)_4^- \rightarrow \\ \rightarrow m\,\{M[Al(OH)_4]_2\} \cdot n\,M(OH)_2 + m\,CaCO_3.$$

Table 1. Composition of the MHC and MHA, the ratio MO/Al_2O_3 in the MHA, and the composition of the thermal decomposition products of the MHA.

MHC $mMCO_3.nM(OH)_2$	MHA $M_{m+n}Al_{2m}(OH)_{8m+2n}$	MO/Al_2O_3	MHA thermal decomposition products $nMO + mMAl_2O_4$, n/m
M = Ni, $m = 1$, $n = 1$	$Ni_3Al_2(OH)_{12}$	3:1	2:1
M = Co, $m = 1$, $n = 2$	$Co_3Al_2(OH)_{12}$	3:1	2:1
M = Cu, $m = 1$, $n = 1$	$Cu_2Al_2(OH)_{10}$	2:1	1:1
M = Zn, $m = 2$, $n = 3$	$Zn_5Al_4(OH)_{22}$	5:2	3:2
M = Zn, $m = 1$, $n = 3$	$Zn_4Al_2(OH)_{14}$	4:1	3:1

The hydroxoaluminates $m\{M[Al(OH)_4]_2\}.nM(OH)_2$ can be represented as $M_{m+n}Al_{2m}(OH)_{8m+2n}$. Thus depending on the composition of the MHC, the products are different MHA with different ratios MO/Al_2O_3, which determine the composition of the thermal decomposition products (see Table 1). Table 1 shows that: a, the composition of the MHA depends markedly on the composition of the MHC; b, the ratio MO/Al_2O_3 in the MHA is always greater than 1; c, the molar ratio $MO/M'Al_2O_4$ in the thermal decomposition products of the MHA, that is the ratio of the free metal oxide to the spinel, is exactly equal to n/m. If the exchange of the ions CO_3^{2-} and AlO_4^- in incomplete, its products will be hydrated metal carbonatoaluminates, and since the number of AlO_4^- ions introduced into the structure is lowered, the ratio MO/Al_2O_3 will be increased.

III. Carriers and adsorbents based on cements

A source of calcium–aluminium carriers and adsorbents is provided by calcium mono- and dialuminates $CaAl_2O_4$ (CA) and $CaAl_4O_7$ (CA_2), which are the principal phases in high-alumina cements. The first stage in the preparation of these carriers is

hydration, which at elevated temperatures gives mainly $Ca_3[Al(OH)_6]_2$ (C_3AH_6):†

$$3CaAl_2O_4\,(CA) + 12H_2O = Ca_3[Al(OH)_6]_2\,(C_3AH_6) + 4Al(OH)_3 \quad (8)$$

$$3CaAl_4O_7\,(CA_2) + 21H_2O = Ca_3[Al(OH)_6]_2\,(C_3AH_6) + 10Al(OH)_3 \quad (9)$$

At lower temperatures, the less stable products C_2AH_8 and CAH_{10} are formed. The compound C_3AH_6 [31] can be obtained either from Ca and Al hydroxides or from the metastable C_2AH_8 and C_4AH_9, which at 25 °C are readily converted into stable C_3AH_6. Amorphous $Al(OH)_3$ is the primary hydration product of calcium aluminates.[31] With the passage of time, that is on ageing, at a suitable pH, amorphous $Al(OH)_3$ crystallises, forming boehmite and hydrargillite (gibbsite).[31,32] Thermodynamic analysis of the hydration of calcium aluminates[9,31–34] confirms that reactions (8) and (9) are possible. The hydroxide $Al(OH)_3$ is formed in the hydration of C_3A, $C_{12}A_7$, CA, and CA_2, and $Ca(OH)_2$ is formed in the reaction of $C_{12}A_7$ with water. Highly basic hydrated Ca aluminates are formed by the reaction of Ca and Al ions in solution and in phase transformations of hydrated calcium aluminates involving OH^-; part of the Al passes into solution as anions. With increase in the basic character of the hydrated Ca aluminates, the probability of their formation increases. Reactions involving $Al(OH)_3$ are thermodynamically more favourable than those with aluminate anions. During hydration and on ageing, the unstable compounds are converted into more stable compounds,[9] in particular into C_3AH_6. The thermal decomposition of hydrated calcium aluminates, the hydration products of anhydrous calcium aluminates, at different temperatures gives $C_{12}A_7$, CaO, Al_2O_3, $Ca(OH)_2$, and other compounds containing Al and/or Ca.[2,7,9,12,15,16,23,32–37] A method has been developed for obtaining the carrier and adsorbent galyumin with a highly developed surface based on calcium monoaluminate (CA).[12,38] X-Ray diffraction has shown that the hydration of CA gives hydrated calcium aluminates, $Al(OH)_3$, and $CaCO_3$; the latter is produced by the reaction of CA with atmospheric CO_2 and with carbonate-containing reagents. To produce an adsorbent with the most highly developed surface, it is necessary to intensify the hydration processes throughout the entire volume of the CA, to break down the layer of $CaCO_3$ and $Al(OH)_3$, and also to extract part of the Ca. The adsorbent and catalyst (galyumin) obtained has not only a highly developed surface (the specific surface increases from 2–4 $m^2\ g^{-1}$ to 400 $m^2\ g^{-1}$, that is by two powers of ten), but also a high mechanical strength.

The aluminium–calcium components of the catalysts have been studied.[39] In one series of experiments, the hydration of CA according to Eqn. (8) was carried out, and the $Al(OH)_3$ formed was combined with the calculated quantity of $Ca(OH)_2$ to give C_3AH_6. In another series of experiments, C_3AH_6 was synthesised by the direct reaction of $Al(OH)_3$ with $Ca(OH)_2$. Thermal decomposition of C_3AH_6 gave the product $12CaO.7Al_2O_3$, that is $Ca_{12}Al_{14}O_{33}$, or $C_{12}A_7$. Some authors[40–42] suggest that water in quantities not less than 1.4% is retained in the $C_{12}A_7$ structure up to high temperatures (1000–1100 °C), and that $C_{12}A_7$ in fact has the composition $12CaO.7Al_2O_3.H_2O$. The properties of $C_{12}A_7$ are such that this water is assumed to be "zeolitic". According to Mamaeva and co-workers,[39] the phase $C_{12}A_7$ is produced at 400 °C; its concentration increases continuously with increase in the heating temperature to 1000 °C. This phase has a highly developed surface, which is preserved even at 800–1000 °C. The higher the degree of dispersion of the phase C_3AH_6 in the unheated specimens, the higher the specific surface (S_{sp}) of the product $C_{12}A_7$ after heating. The data obtained[39,43] have been used to develop a method for obtaining an aluminium–calcium carrier and adsorbent (galyumin-Ts) with a thermally stable texture (withstanding thermal treatment at 600–1000 °C) and a mechanical strength up to 500–700 kg cm^{-2}.

A study of the infrared spectra[44,45] of a number of calcium aluminates (CA, CA_2, $C_{12}A_7$) and catalysts and adsorbents based on them, with different S_{sp} (30–400 $m^2\ g^{-1}$), showed that the bands in the range 400–900 cm^{-1} are due to the vibrations of aluminium–oxygen tetrahedra in the framework zeolite-like structure. The calcium ion apparently acts as compensating cation. Depending on the method of preparation, the value of S_{sp}, and the concentration of CaO, the aluminium–calcium adsorbents and catalysts can be divided into two groups: a, those with a framework structure containing calcium aluminates; and b, those consisting chiefly of γ-Al_2O_3 modified by calcium. The water in the aluminium–calcium adsorbents and catalysts is present in different states; it may be adsorbed, form surface OH groups, and be present as $Ca(OH)_2$, $Al(OH)_3$, and hydrated calcium aluminates. From an analysis of infrared data on the hydration of the calcium aluminates CA, CA_2, C_3A, and $C_{12}A_7$,[9,46] it was suggested that the high strength of cement block is achieved as a result of the formation of Al–O–Al structural bonds between the octahedra of aluminium hydroxide and hydrated calcium aluminates. The highly developed thermally stable porous structure of an adsorbent based on calcium aluminates (novogal), and the possibility of controlling this structure, open up the possibility of using novogal for the gas-chromatographic separation of complex mixtures of C_1–C_4 hydrocarbons.[47,48] From the nature of its reaction with an adsorbate, novogal must be classified as a specific adsorbent of type II.[49]

The genesis of the phase composition and texture of a carrier, adsorbent, and catalyst based on calcium–aluminium cement (talyum), whose mineralogical components are CA and CA_2, have been studied.[50] When talyum is treated with water under the conditions of the preparation of cement-containing catalysts, the original phases (CA, CA_2) dissolve in the first stage (the mixing stage), after which the nuclei of metastable (C_2AH_8, C_4AH_{13}) and stable (C_3AH_6, gibbsite) hydrated new formations separate from the supersaturated solution. The fact that the hydration product of Al_2O_3 is produced in the hydration of aluminium–calcium cements and subsequent thermal decomposition provided the starting point for the production and study of two-component γ-Al_2O_3–CA and γ-Al_2O_3–CA_2 compositions.[51,52] Their mechanical strength reaches 1450 kg cm^{-2} and 1000 kg cm^{-2} for the compositions 40% CA–Al_2O_3 and 20% CA–Al_2O_3 respectively. The highest mechanical strength corresponds to the texture in which a maximum contribution to S_{sp} is made by the narrow pores, and a minimum contribution by the wide pores.

The processes taking place in the production of catalysts based on calcium aluminates have been studied by high-resolution ^{27}Al NMR.[53] The structure of anhydrous calcium aluminates (CA, CA_2, C_3A, $C_{12}A_7$, talyum) contain aluminium–oxygen tetrahedra; the aluminium atoms in the tetrahedra are of different types, and their non-equivalence increases on going from highly basic to weakly

† The following notation is used in the chemistry of cements: C = CaO, A = Al_2O_3, H = H_2O.

basic aluminates. On hydration, which is one of the stages of the production of aluminium–calcium catalysts and carriers, the process $[AlO_4] \rightarrow [AlO_6]$ takes place, and the process $[AlO_6] \rightarrow [AlO_4]$ takes place on thermal decomposition. The non-equivalence of the aluminium atoms in tetrahedral coordination decreases, and the ratio $[AlO_4]/[AlO_6]$ decreases with increase in the degree of hydration. The presence of a framework of aluminium–oxygen $[AlO_4]$ tetrahedra in anhydrous calcium aluminates makes their structure similar to that of zeolites.[44,45] For zeolites, Loewenstein's rule applies; according to this rule, two aluminium atoms in tetrahedral coordination should not have a shared oxygen atom. The structure of calcium aluminates clearly indicates that Loewenstein's rule is not universal.[54] A quantum-chemical analysis of this rule for aluminium-containing catalysts and adsorbents[55] showed that a structure in which two $[AlO_4]$ tetrahedra have a shared oxygen atom is stabilised by a metal ion acting as compensating cation. The reactivity of calcium aluminates with respect to water, which is of considerable importance in the production of aluminium–calcium catalysts, also depends on distortions in the oxygen environment of calcium, and in particular on the Ca–O distances; the shorter this distance, the higher the reactivity of the calcium aluminate with respect to water.[53] Thus the rate of hydration decreases in the order $C_3A < C_{12}A_7 < CA < CA_2$,[56] and the shortest Ca–O distance increases in the same order from 2.26 Å to 2.33 Å.

Thermal desorption, thermal analysis, and X-ray diffraction have been used to study the reaction of water vapour with the aluminium–calcium components of catalysts based on calcium aluminates.[57] The presence of $C_{12}A_7$ is responsible for the increased adsorption of water vapour and the specific form of the thermal-desorption spectrum. The reaction of water vapour with the aluminium–calcium components of the catalysts, unlike the liquid-phase reaction, is not accompanied by a change in the phase composition, and this makes possible the extensive use of these catalysts in gas-phase processes involving water. Millimetre-wave spectroscopy has shown[58] that in the liquid phase, the quantity of immobilised water in $C_{12}A_7$ is more than 100 times the capacity of a monolayer, and this has been attributed to the filling of the cavities in the structure and the superposition of the chemical reaction of $C_{12}A_7$ with water on the adsorption process. The increase in the rate of hydration of aluminate cement[32] with increase in its degree of dispersion is due both to an increase in the surface area and to activation of the reacting particles. The last factor may predominate, as observed in the mechanical activation of calcium aluminates by treatment in mills without change in the degree of dispersion.[59]

Infrared spectroscopy in diffuse scattered light has been used to study the hydroxyl covering and adsorption centres of aluminium–calcium catalysts and carriers with a highly developed surface.[60] The presence of surface OH groups of several types was established. A quantitative infrared spectroscopic study of the basic and acidic (aprotic) centres from the adsorption of deuteriochloroform and CO respectively[61,62] revealed the existence on the surface of two types of aprotic acidic centre, one of which was combined with Ca ions (type I), and the other with Al ions (type II). With increase in the degree of hydration of the calcium aluminates, the concentration of the centres of type I decreases more extensively than that of the centres of type II, corresponding to the greater degree of displacement of calcium ions from the lattice, compared with aluminium ions. Three types of basic centre were detected: the strength of the centres of one type is similar to that of the basic centres in γ-Al_2O_3; other stronger centres correspond to the oxygen in the Al–O–Ca structure; and, finally, the third and strongest centres correspond to the oxygen in the Ca–O structure. According to Sominskii and co-workers,[17,52,63–65] calcium aluminates with a highly developed surface (galyumins) also show Brönsted acidity, detected using butylamine and pyridine; the adsorption of pyridine and acetone also detected Lewis centres, and the adsorption of hexadeuterioacetone detected basic centres. A thermally stable catalyst carrier[66] and an adsorbent[67] are obtained from Al hydroxides and Ca oxide, hydroxide, and carbonate. A carrier based on calcium aluminates has a high S_{sp} and is suitable for use over a wide temperature range, 400–900 °C.[68] Calcium aluminates with a highly developed surface and a high reactivity can be obtained directly from molten Al and Ca nitrates,[69] that is by simple mixing using effluent-free technology.[38,39,43,48,50,51] Thermal-desorption studies of the adsorption of CO_2, H_2O, O_2, and H_2 on calcium aluminates with different CaO/Al_2O_3 ratios and different phase compositions (CaO, C_3A, $C_{12}A_7$, CA, CA_2)[70] indicate that the adsorption bonds are extremely strong. Thus H_2O is desorbed at 930 °C ($C_{12}A_7 . H_2O$), O_2 at 720–825 °C, and CO at 450 °C and 600–760 °C.

Ca, Sr, and Ba aluminates have much in common; they all have high melting points and similar densities, mechanical strength, and tendency to undergo hydration. They are therefore all used in the same way in the production of ceramics, binding agents, and sintering cements.[35] A significant feature is that the crystal structures of the alkaline earth metal monoaluminates are based on $[AlO_4]$ tetrahedra sharing oxygen atoms.[35,71,72] The aluminate $SrO.2Al_2O_3$ is a structural analogue of $CaO.2Al_2O_3$,[35,73] and $3CaO.Al_2O_3$, $3SrO.Al_2O_3$, and $3BaO.Al_2O_3$ are also isostructural.[35] Carriers and adsorbents based on Ca, Sr, and Ba aluminates should therefore show similar behaviour. Thus the addition of Ca, Sr, and Ba oxides to γ-Al_2O_3 decreases sintering and leads to the preservation of a comparatively highly developed surface on formation of the corresponding aluminate.[74–76] The great importance of zeolites in catalysis is drawing attention to cement–zeolite compositions.[77–79] Binders with different compositions based on Portland cement gain strength rapidly, have a high resistance to wear, and can be used to encapsulate sorbents and catalysts.[80] A composition using natural zeolites appears promising.[81–83] Mixed cements containing zeolite have a high strength.[81,82] The use of Portland cement as binding agent makes it possible to obtain granulated NaA zeolites with a high mechanical strength, minimum secondary porosity, and high adsorbing power.[84]

IV. The production of metal-cement catalysts

The formation processes have been studied most intensively for nickel-cement catalysts, which are widely used in the hydrogenation of oxides of carbon, the decomposition of ammonia, the conversion of methane, the hydrogenolysis of glucose, etc.[1,2,3,6,85–87] Thus the synthesis of ammonia in plants with high unit output involves the production of synthesis gas by the conversion of methane and purification on nickel contact catalysts. The production of ammonia and hydrogen alone uses up about 30% of the total world production of catalysts. Cements are used to obtain nickel-cement contact catalysts in three ways: a, calcium aluminates are used as one of the chemical reagents reacting with the source of the active component; b, calcium aluminates are added to the catalyst mass as a binding agent to produce a strong hardened structure by moist-air treatment (MAT) or hydrothermal treatment (HTT); and c, to

combine the processes of contact catalyst formation and hydration hardening of the calcium aluminates, the original components are mixed to give a uniform mixture (alternatively, the mixing is carried out at low liquid : solid ratios), which in the form of tablets are subjected to HTT.[19,20,22,23,88–90] The reactions described by Eqns. (1)–(4) take place in the liquid medium.[7,14,89–91] In the presence of Ni salts, the phases C_2AH_8 and CAH_{10} are not detected. With increase in the ratio Ni salt/cement (CA, CA_2 talyum), the quantity of $CaCO_3$ formed increases, $Ca(OH)_2$ disappears, and $Ni(OH)_2$ appears. In complete accordance with Eqn. (3), with increase in the concentration of nickel hydroxide carbonate, the quantity of $CaCO_3$ (criterion of the exchange reaction) and S_{sp} (criterion of the development of the surface) pass through a maximum.[8] The CO_3^{2-} ion evidently does not enter the structure of the hydrated aluminate, since if a compound of the type $M_3[Al(OH)_4(CO_3)]_2$ were formed, the $CaCO_3$ concentration would have decreased and would differ significantly from that calculated from Eqn. (3). The reactions between calcium aluminates and Ni hydroxide carbonate can take place by a liquid-phase or a solid-phase mechanism, depending on the composition of the medium (water, aqueous ammonia solution) and the liquid : solid ratio. The Ni hydroxoaluminate formed in reactions (3) and (4) decomposes when heated according to Eqn. (5) to give a poorly crystalline disordered $NiO-Al_2O_3$ solid solution, whose structure is perfected at 400–1000 °C, accompanied by the gradual liberation of the excess NiO.[90] Ni hydroxoaluminate is the main form in which the active component exists in the catalysts at the stage preceding thermal decomposition and activation. Since the reaction of the components is limited by the rate of solution of the calcium aluminates (talyum) in aqueous ammonia solution, an effective method of increasing the extent of the reaction is by increasing the degree of dispersion and the ratio CA/CA_2.[92] On thermal treatment, the phase CaO formed by the high-temperature decomposition of $CaCO_3$ reacts with Al_2O_3, preventing the reaction of the superstoichiometric NiO with Al_2O_3 and decreasing the rate of formation of spinel ($NiAl_2O_4$).[92] The specific surface of the nickel catalysts is determined by the value of S_{sp} of the dispersed phase of the $NiO-Al_2O_3$ solid solution. High-temperature X-ray diffraction has shown that nickel–aluminium–calcium catalysts are reduced in two stages, at 400–600 °C and 600–800 °C. The presence of compounds difficult to reduce ensures the preservation of a high degree of dispersion of metallic nickel over a wide temperature range and creates conditions for the effective use of aluminium–calcium-based catalysts in high-temperature processes (conversion of hydrocarbons, decomposition of NH_3). A composition containing CA, CA_2, and Al_2O_3 together with nickel can be used to produce an optimum catalyst for low- and high-temperature processes.[89–91] According to Dzis'ko,[4] mixing does not make it possible to achieve the same extent of reaction between the components as the combined precipitation of $Ni(OH)_2$ and $Al(OH)_3$ and the coprecipitation of $Ni(OH)_2$ on an Al_2O_3 carrier. The nickel–aluminium–calcium system (and, as shown below, all other systems based on calcium aluminates) is an exception to this rule. In this case the product is formed by a new mechanism, in which the original components, on chemical mixing, react with one another practically completely under very mild conditions:

$$\begin{array}{c} Ni_3CO_3(OH)_4\cdot 4H_2O + CaAl_2O_4 + CaAl_4O_7 \rightarrow \\ \rightarrow Ni_3Al_2(OH)_{12} + CaCO_3 + Al(OH)_3 \\ \downarrow 350^\circ C \qquad\qquad \downarrow 740^\circ C \qquad \downarrow 300^\circ C \\ (NiO)_3{-}Al_2O_3 \qquad\quad CaO \qquad Al_2O_3 \\ \downarrow 400\text{–}1000^\circ C \qquad\quad \downarrow 800\text{–}1000^\circ C \\ x\cdot NiO + (NiO)_{3-x}\cdot Al_2O_3 \qquad\quad CaAl_2O_4 \end{array} \qquad (10)$$

X-ray diffraction, texture, thermochromatographic, and spectral studies[90,93–99] confirm that a multiphase system with a highly developed surface is formed. Change in the ratio of Al_2O_3, CA, and CA_2 [89,90] makes it possible to control the degree of dispersion, phase composition, and mechanical strength of Ni catalysts. The plastic deformation of $CaCO_3$ on pressing leads to an increase in the unit contact strength; the mechanical strength increases with increase in the $CaCO_3$ concentration. The sharp increase in strength at high pressing pressures (800–1000 MPa)[100] indicates plastic deformation of the structure-forming particles, in particular calcite. The increased strength of the bond between NiO and the carrier is confirmed by the thermal-vacuum electrical conductivity curves.[101]

V. Catalysts for the methanation of oxides of carbon

In the catalytic purification of technical gases (nitrogen–hydrogen mixture, hydrogen, etc.) from CO and CO_2, the concentration of oxides of carbon at the outlet should not exceed 10–20 $cm^3\ m^{-3}$ (10–20 p.p.m.). The catalytic purification from CO and CO_2 is based mainly on their exothermic hydrogenation to CH_4 (so-called methanation). Methanation can be carried out for different purposes: to remove poisons (CO, CO_2), to obtain a fuel gas, and to transfer the heat of hydrogenation to a distance.[1,102,103] The most suitable catalysts for purifying hydrogen-containing gases from CO and CO_2 are nickel catalysts; they are more active and more selective than iron catalysts, and less expensive than contact catalysts based on the Pt group metals.[85,86,102] Catalysts for purification from CO and CO_2 must satisfy severe requirements in relation to: a, activity; b, thermal stability (the activity should be preserved on superheating, which usually takes place with an increased concentration of CO_2 and CO at the inlet); c, stability, that is resistance to the action of the reaction medium; and d, mechanical strength. Mechanical strength is particularly important when large quantities of catalyst, up to 50 tons, are loaded into the methanation vessels in plants with a high unit output (in particular in NH_3 synthesis plants with an output of up to 1360 tons per day). These requirements are satisfied by Ni contact catalysts based on cement (aluminium–calcium).[7,14,89–91,102,104–115] By selecting the reaction medium, it is possible to control the ratio between the oxide and metallic phases.[93,97] An important part in the production of the contact catalysts is played by the change in the oxygen coordination of aluminium from tetrahedral (Al_t) to octahedral (Al_o) on hydration and from Al_o to Al_t on thermal treatment.[16,98]

The reduction of nickel–aluminium–calcium contact catalysts to give a metallic nickel phase involves several stages. The low-temperature stage (160–400°) involves the reduction of free nickel oxide, and the high-temperature stage involves the reduction of

combined oxide. The second stage may be necessary for the following reasons: a, the difficulty of reducing nickel in CaO–NiO solid solutions; b, the formation of nickel aluminium spinel; and c, the replacement of the metal ion in the zeolite-like structure of the aluminates. The principal form of existence of the precursor of the active form of nickel is nickel hydroxoaluminate, which on thermal decomposition is converted into $NiO-Al_2O_3$ solid solutions.[90] There is restricted mutual solubility of the components, however, in the NiO–Ca(Ba)O system.[116–118] Extensive reaction of nickel oxide with calcium aluminates does not give contact catalysts with a high activity in low-temperature hydrogenation processes. To avoid this limitation, Al_2O_3 is added to the catalyst together with calcium aluminates.[119] The NKM-4 (4A) catalysts obtained in this way can operate at temperatures much lower than the minimum working temperatures (260 °C) for the hydrogenation of CO and CO_2, used in the large-scale production of ammonia.[8,9,108,119] Electron microscopy has shown the decisive part played by the carrier in the distribution of the particles of reduced Ni at temperatures in the range 400–800 °C.[120] Simplex lattices have been used to construct composition–property (total specific surface, surface area of the active component, S_{Ni}, mechanical strength) diagrams to find the optimum ratio of the components NiO, Ca, CA_2, and Al_2O_3.[121] It was found that the NiO–talyum reaction has a greater influence on S_{sp} than the $NiO-Al_2O_3$ reaction; the value of S_{Ni}, on the other hand, depends to a greater extent on the distribution of nickel in Al_2O_3. The change in the strength of the catalyst during hydrothermal treatment is due to the characteristics of the hardening of the binding component (cement); hydration is accompanied by the appearance of micro-strains produced by the crowded growth of the crystals of the new formations.[122] The increase in strength when the contact catalyst is heated to 400° is due to the relaxation of the strains produced on hydrothermal treatment.[123,124] The low-temperature decomposition of $CaCO_3$ has been detected in nickel-cement catalysts in which calcite appears during preparation, at temperatures $\leqslant$400 °C in reducing media.[125,126]

The purification of technical gases from CO and CO_2 on Ni contact catalysts has been studied by Kreindel' and co-workers.[127–129] In the kinetic range, the specific catalytic activity (calculated for 1 m^2 Ni) is constant and independent of the nature of the carrier, the method of preparation, and the temperatures of thermal treatment and reduction of the catalysts. With increase in temperature, the reaction passes into the outer-diffusion range.

The kinetics of the methanation of CO and CO_2 and their mixtures on the industrial nickel–aluminium–calcium catalyst[108] have been studied.[130–138] The principal kinetic characteristics of the methanation of CO are the same at atmospheric pressure and at an increased pressure (up to 3 MPa). In the combined methanation of CO and CO_2, the components have a simple influence on one another, with adsorption competition on the surface. Mass spectrometry, thermal desorption, infrared spectroscopy, and isotope studies[134–136] showed that the mechanism of the methanation does not involve the dissociative adsorption of CO and CO_2; the reaction takes place with the formation of compounds $C_xH_yO_z$ involving atomic adsorbed hydrogen. The data obtained[130–136] made it possible to put forward a new stepwise scheme for the hydrogenation of CO and CO_2, according to which both processes take place without the preliminary dissociation of CO and CO_2. In the methanation of carbon monoxide, the surface is covered by CO, and also HCO, HCOH, CH, and OH; the limiting stage is the reaction of $CH_{(ads)}$ with $H_{(ads)}$. In the methanation of CO_2; the slow stage is the reaction of $CO_{2(ads)}$ and $H_{(ads)}$, and intermediate compounds $C_xH_yO_z$ are present on the surface. These results show good agreement with published conclusions.[103,137,138] The nickel-cement catalysts NKM-4A and GIAP-16 are highly active in the methanation of stoichiometric mixtures of CO and CO_2 with H_2 in the temperature range 300–700 °C;[139] this is of undoubted interest for solving the problem of the transfer of energy over large distances by a combination of exothermic and endothermic reactions (an "Adam and Eve" process).[11]

VI. Catalysts for the conversion of hydrocarbons

One of the indicators of technical progress in developed countries is the level of output in the production of hydrogen. In recent decades, the world production of hydrogen has increased several-fold. This is due to the increase in the production of ammonia, methanol, and the products of petrochemical synthesis, and the vast contribution made to these processes by reactions involving hydrogen. One of the most widely encountered methods for obtaining hydrogen-containing gases is by the catalytic conversion of hydrocarbons.[86,140–142] The steam conversion of methane takes place at high temperatures (800–900 °C), and this naturally makes increased demands on the catalysts and makes it necessary to avoid carriers based on SiO_2, which can be carried away by the steam and deposited on the cold parts of the equipment. As a result, extensive use has been made of nickel catalysts on alumina cements, calcium aluminates, and Al_2O_3 containing alkaline earth metal oxides as promoters.[87,140,141] High-temperature treatment of the carrier or catalyst mass leads to the formation of Ca, Sr, and Ba aluminates in the surface layers or throughout the entire volume of the contact catalyst. To avoid coke formation on catalysts in the conversion of hydrocarbons, attempts were made to introduce a hydraulic cement as early as the nineteen-thirties.[143] The introduction of cements into a mixture of nickel salts and activators gave catalysts with a successful combination of high mechanical strength, stable activity, and resistance to coke formation.[144] A cement-containing nickel catalyst with a high mechanical strength (400 kg cm^{-2}) has been described.[145] The most active catalysts for reforming CH_4 with steam or a mixture of steam and O_2 are contact catalysts including Al_2O_3, CaO, and NiO.[146,147] A catalyst based on alumina with added Ca and Mg oxides has an increased thermal stability and mechanical strength.[147] An Ni/Al_2O_3 catalyst promoted by CaO is used for the steam conversion of petroleum.[148] Nickel-containing contact catalysts produced in the USSR are being used successfully: GIAP-16 (24–26% NiO, 55–59% Al_2O_3, 14–16% CaO, 0.8–1.2% BaO) and KSN-2 (12–15% NiO, 80–83% Al_2O_3, 3% CaO, 1% MgO).[85,149] The use of nickel on a cement carrier makes it possible to carry out the steam reforming of C_2 and higher hydrocarbons with a low steam consumption without coke formation.[150] A mechanically strong catalyst with a long working life and high activity in the steam reforming of hydrocarbons contains a mixture of calcium aluminates and nickel, promoted by a Ba salt.[151] The nickel catalysts based on calcium aluminates C11-2, C11-5, and C11-25 [152] were developed for the steam conversion of petroleum fractions, where there is a danger of extensive coke formation on the contact catalysts and it is necessary to use high steam/hydrocarbon ratios. A stable catalyst for the reforming of hydrocarbons with steam, resistant to coke formation, contains an aluminate cement and a mixture of Ni and Mg oxides.[153] The activity and specific surface of nickel–aluminium–calcium catalysts increase with increased concentrations of Al_2O_3 and

CaO.[154] The effective high-temperature catalyst GIAP-16N for the conversion of CH_4 with steam is obtained by introducing CA, CA_2, and high-alumina cements into a spent nickel–aluminium hydrogenation catalyst.[155] The presence of free CaO in a composition containing NiO and an aluminate cement[156–160] apparently makes it possible, by hydration at 5–35 °C and thermal treatment at 550–1200 °C, to bind free Al_2O_3 and thus to avoid the formation of nickel aluminium spinel, difficult to reduce. The GS-12 catalyst for the conversion of methane[161] is obtained by depositing nickel on Al, Ba, and Ca oxides sintered at 1300 °C, when aluminates are formed. This catalyst can operate at high natural-gas loads and lowered steam/gas and O_2/CH_4 ratios. The residual concentration of CH_4 in the gas is 0.2–0.4%. The cement-containing catalysts for the conversion of methane, GIAP-16 and GIAP-16-2, produced in the Soviet Union, are widely used in large-scale plants for ammonia production; many of the characteristics of GIAP-16-2 match those of the CCI contact catalyst C-11-4.[162–164]

Alumina cements are often used as binding agents.[165,166] X-Ray diffraction has detected the presence of CA_6 in the nickel catalyst KSK-2 on a carrier modified by CaO or MgO.[167,168] A mixed nickel catalyst containing alumina and a fused alumina cement[169] is used to obtain H_2 from hydrocarbons with boiling points below 150 °C. Natural gas is purified from methane homologues by steam conversion at 300–400 °C in the presence of a nickel–chromium catalyst promoted by CaO and Al_2O_3.[170] An extremely productive idea has been put forward for creating a flexible technology for the production of nickel cement-containing contact catalysts for low-temperature (methanation) and high-temperature (methane conversion) processes.[1,114] An equally promising suggestion is that spent methanation catalysts be used as raw material for the preparation of GIAP-16 cement-containing contact catalysts for the conversion of CH_4.[155,171] Catalysts for the conversion of heavy petroleum residues, where the principal components of the catalysts are the calcium aluminates $C_{12}A_7$ and C_3A, have been developed.[172] The development of chemothermal methods for transferring energy over long distances using a cycle involving the steam conversion of methane and the hydrogenation of oxides of carbon required the development of thermally stable contact catalysts containing calcium aluminates.[173–175] Thermally stable and mechanically strong Cu–Ni,[176] V,[177] Rh,[178,179] Fe,[180] and Co–Mn [181,182] catalysts on an aluminium–calcium base for the conversion of hydrocarbons are also known. The base is provided by $C_{12}A_7$, CA_6, CA, CA_2,[177] and C_3A.[181] Ba aluminates, like Ca aluminates, are used successfully to produce Ni conversion catalysts.[183–185] The thermal stability of γ-Al_2O_3 is increased when its surface is modified by CaO, SrO, and BaO,[186] apparently as a result of the formation of surface layers of aluminates. With increase in the concentration of the alkaline earth metal oxides in Al_2O_3, the number of electron-donor centres increases, and this was assumed[187,188] to be related to the increase in the rate of the transformation of CH_4 in the presence of water vapour on promoted Ni catalysts. The presence of a large quantity of basic and reducing centres on the surface of aluminium–calcium carriers or Al_2O_3 modified by CaO leads to the suppression of coke formation on Ni catalysts for the conversion of hydrocarbons.[189] CaO–NiO specimens obtained by the thermal treatment of the $Ca(OH)_2$–$Ni(OH)_2$ system have a micro-structure differing markedly from that of their mechanical mixture; this is attributed to the hindered crystallisation of the oxides in the presence of one another.[189] CaO–NiO, CaO–Al_2O_3, and NiO–Al_2O_3 reactions apparently take place in nickel–aluminium–calcium conversion catalysts. In the NiO–Al_2O_3 system, even after high-temperature treatment (600–900 °C), three oxide phases are preserved: $NiAl_2O_4$ and two nickel oxides, one of which, which has a disordered crystal lattice, contains an appreciable quantity of Al ions;[190] these ions, after reduction of the catalyst, facilitate the formation of Ni crystallites with an extremely high thermal stability. Magnetic studies[191] of Ca^{2+}-promoted nickel–aluminium contact catalysts for the steam reforming of petroleum established that the reaction of metallic Ni with C_3A_5 prevents the migration of Ni over the surface and the formation of large crystallites. The high-temperature forms of adsorbed water (in $C_{12}A_7$) and oxygen may play an important role in hydrocarbon reforming processes.[70] The best carriers are calcium–aluminium cements, treated with the reaction mixture under reforming conditions and containing the phases $C_{12}A_7$ and CA.[192] When evaluating the role of individual components, it is necessary to take into account the fact that the MO–Al_2O_3 compositions (M = Ca, Sr, Ba) catalyse the reaction of hydrocarbons with steam, leading to the formation of CO and CO_2, and at the same time suppress the formation of carbon deposits.[193]

The physicochemical principles of the production and action of nickel–aluminium–calcium catalysts for the conversion of CH_4, examined briefly above, are described more fully elsewhere.[90,91,93–99,122,123] The stability and texture of catalysts are related to their phase composition.[91] It is possible to lower the Ni concentration while preserving the high activity of the contact catalyst as a result of the highly developed surface and the lowered tendency to form spinel.[194] The presence of NiO in the combined state is a condition for obtaining a thermally stable and active catalyst.[114,195] The degree of dispersion and stability of the active phase (Ni phase) depend markedly on the composition and structure of the calcium aluminate cement support.[196] Impregnating a γ-Al_2O_3 carrier with Al and Ca salts to give different calcium aluminates leads to development of the surface, stabilisation of the degree of dispersion, and increase in the stability and resistance of the catalyst to coke formation.[197]

VII. Catalysts for obtaining protective atmospheres

Controlled (protective) atmospheres and reducing media, obtained by the dissociation (cracking) of ammonia and not containing CO and hydrocarbons, are widely used in metallurgy, mechanical engineering, chemistry, and other branches of the national economy.[198–200] Protective inert atmospheres are used to prevent the oxidation and change in the chemical composition of the surface of a metal, in hot zinc plating, electrochemical tin plating, the deposition of coatings, the production of glass, and the treatment of gold and other metal articles. Throughout the world, the dissociation of ammonia is carried out in the presence of iron- and nickel-containing contact catalysts.[198–201] Catalysts for the dissociation of ammonia have to satisfy severe requirements: working temperatures 600–950 °C, concentration of residual $NH_3 \leqslant 0.05$–0.1% at volume velocities of 500–2000 h^{-1}. KDA-5 and KDA-10A nickel catalysts for the dissociation of NH_3 contain cements as components.[108,202] KDA-5 [202] is obtained by mixing nickel hydroxide carbonate (NHC) (20–50% NiO) with calcium aluminates and 25% aqueous ammonia solution. At 800 °C the residual concentration of ammonia decomposing on this catalyst (at a volume velocity of 1000–2000 h^{-1}) does not exceed 0.02–0.025% (equilibrium value 0.013%). In the production of the KDA-10 A catalyst,[108] cements are used together with Al_2O_3, making it possible to combine high activity of the contact catalyst with mechanical

strength and thermal stability. Calcium aluminates have been used as hydraulic binding agents in the production of the nickel contact catalysts KDA-3,[203] KDA-4,[204] and KDA-7.[205] The use of a combination of the properties of calcium aluminates, as components of catalytic compositions and as hydraulic binding agents, forms the basis of the nickel dissociation catalyst NKM-2A.[90,91,114] NHC, calcium aluminates, and aqueous ammonia solution are mixed at the lowest possible liquid : solid ratio (0.2–0.3). At the mixing stage, the reactivity of the cements ensures their reaction with NHC. The use of a low liquid : solid ratio made it possible to preserve most of the catalyst mass in the non-hydrated form, and to make use of the binding properties of the cements at the stage of hydrothermal synthesis and HTT. The high degree of binding of nickel in the NKM-2 catalyst ensures a lowered concentration of NiO, and the nickel phase is stable both to sintering and to binding in nickel aluminium spinel. Experience in the production and use of controlled atmospheres in ferrous metallurgy indicates the promising possibilities provided by iron-containing contact catalysts. A thermally stable catalyst should contain a refractory component, for example cements ($CaAl_2O_4$ melts at 1600 °C, and $CaAl_4O_7$ at 1750 °C). Calcium aluminates can be added either directly or as components which act as sources of Ca and Al. In the production of Fe contact catalysts by fusion, temperatures of 1500–1700 °C are sufficient for the formation of the compounds $Ca_xAl_yO_z$. Fe-containing KDA-1A,[206] KDA-2,[207] and KDA-1M[208] catalysts for the dissociation of NH_3 are obtained in this way. These catalysts contain a solid solution based on magnetite, formed with the participation of $CaAl_2O_4$. This series of catalysts with a high iron concentration (up to 77%) and a high thermal conductivity ensures the decomposition of NH_3 to a residual concentration $\leqslant 0.05-0.1\%$ at 650–950 °C. Experience in the industrial use of KDA catalysts has shown that they are capable of stable operation at temperatures of 700–900 °C and volume velocities of 1000–6000 h^{-1} for not less than 5–7 years, and can withstand brief superheating to 1000–1100 °C.[209] An important and promising development involves the dissociation of NH_3 on metal-cement contact catalysts to give a nitrogen–hydrogen mixture for the reduction of catalysts in the starting-up of assemblies when there are no other sources of hydrogen.[1,209]

VIII. Catalysts for purifying sulphur-containing gases

Sulphur compounds present in technical gases are powerful catalyst poisons, and lead to the corrosion of apparatus and contamination of the atmosphere. Industrial methods for purifying gases from harmful impurities, including sulphur compounds, can be divided into three groups: adsorption, liquid (or absorption), and chemisorption (or chemisorption–catalytic).[85] Zinc oxide absorbers remove H_2S, C_2H_5SH, and COS effectively, and CS_2 less effectively. The absorption of H_2S gives ZnS, which is stable in the reaction medium, so that this reaction is displaced completely to the right. In the production of zinc–aluminium–calcium catalysts, reactions (3) and (4) take place between $CaAl_2O_4$ ($CaAl_4O_7$) and zinc hydroxide carbonate (ZHC) to give zinc hydroxoaluminate (ZHA) and $CaCO_3$.[24,25,52,65] The thermal decomposition of ZHA is described by Eqn. (5). The source of ZnO is ZHA, where the ratio $ZnO/Al_2O_3 > 1$, and also ZHC. The morphology of zinc-cement contact catalysts[28] is characterised by the presence of different structures — block (carrier) and globular (zinc-containing component). The texture of $ZnO-CaAl_2O_4$ and $ZnO-CaAl_4O_7$ catalysts[210] is determined to a large extent by the reaction of the components. The study of the production of zinc oxide absorbers for sulphur-containing gases on $CaAl_2O_4$, $CaAl_4O_7$, and Al_2O_3 carriers[26,52,211] revealed a regular feature: the binding of ZHC in ZHA lowers the activity of the chemisorbing materials to a greater extent, the more extensive the reaction between ZHC and the carrier. The degree of binding of the zinc component in ZHA [26,101,211] decreases in the order $CaAl_2O_4 > CaAl_4O_7 > Al_2O_3 >$ galyumin, whereas the activity increases in this order.[26] Other conditions being equal, the extent of the absorption of H_2S is determined only by the concentration of the free ZnO phase. Zn^{2+} ions in tetrahedral surface centres and bulk zinc aluminium spinel are extremely stable, and this explains the inactivity of the absorbers towards H_2S and the inhibition of sulphidation processes on these contact catalysts.[212] The reaction of C_2H_5SH with absorbers based on ZnO [213] takes place in two stages: ZnS and hydrocarbon are formed initially in the sulphurisation stage, after which degradation hydrogenation, and the synthesis of sulphur-containing compounds take place on ZnS. A thermodynamic analysis[214] has shown that the presence of hydrogen in the reaction mixture prevents the decomposition of the sulphur-containing substances to sulphur, decreases the rate of formation of thiophen and thiophan, and increases the degree of purification to 80–100%. Cement provides an extremely effective means of granulating ZnO.[211,215,216] Calcium aluminates (and also Sr and Ba aluminates) have been used to develop effective zinc-containing contact catalysts for purification from sulphur.[217–219] The catalyst TsKA-1 [217] has a mechanical strength up to 350–500 kg cm^{-2} with a sulphur capacity (400 °C) of 27–33 mass%. The presence of CaO in the cements increases the absorbing power.[220,221] Special-purpose zinc-containing cements are of interest for catalysis.[222–224] One promising method for purifying industrial effluent gases with the simultaneous utilisation of sulphur-containing compounds is provided by the Claus process,[225–227] in which sulphur is obtained using aluminate cements. This process, in particular, uses a wide-pore aluminium-cement catalyst called the Norwegian catalyst.[226] The introduction of the oxides of K, Ba, P, and Ln into catalysts based on high-alumina cements increases the yield of elemental sulphur considerably.[227] A composition containing an alkaline earth metal and aluminium oxide, heated at a high temperature, with S_{sp} = 100–300 $m^2\ g^{-1}$ and a pore volume of 0.30–0.60 $cm^3\ g^{-1}$, has been proposed as an effective sorbent for gases containing SO_x.[228] The extraction of sulphur from SO_2 in flue gases is carried out by reducing the SO_2 with hydrocarbons (CH_4, natural gas) at 450–1300 °C in the presence of calcium aluminates deposited on Al_2O_3.[229]

IX. Catalytic systems for the conversion of CO by water vapour and the synthesis and decomposition of methanol

Copper-containing systems, obtained by deposition, precipitation, or mixing, are extremely effective catalysts for the conversion of CO by water vapour and the synthesis and decomposition of methanol. To maintain the copper-containing component in the active state, it is necessary to use carriers and promoters which are capable of ensuring a uniform distribution of copper in the matrix of stabilising components.

The use of cements has made it possible to obtain catalysts by chemical mixing. The degree of interaction of the components obtained in this way is not less than that obtained by precipitation.

The formation of contact catalysts. The formation of copper-cement contact catalysts has been studied.[52,65,230–233] The catalytic system obtained from copper hydroxide carbonate (CHC) and talyum (CA + CA_2) contains copper hydroxoaluminate, calcium carbonate (as calcite), aluminium hydroxide (as gibbsite), and calcium hydroxide (amorphous to X-rays). The extent of the reaction of CHC with talyum, estimated from the quantities of calcite and gibbsite formed, increases with increase in the fineness of grinding (FG) of talyum, and increases even more strongly with increase in the ratio CA/CA_2.[230,234] The anionic and cationic fractions of CHC have different fates: the carbonate ion is converted into calcite, and the copper ion into copper hydroxoaluminate and $Cu(OH)_2$. At increased temperatures (90 °C), the rate of decomposition of CHC is greater than the rate of its reaction with CA and CA_2; at low temperatures, CA and CA_2 are hydrated slowly, particularly CA_2. On thermal decomposition, copper hydroxoaluminate decomposes to a $CuO-Al_2O_3$ solid solution and CuO. With increase in the heating temperature to 600–800 °C, the spinel $CaAl_2O_4$ is formed from the solid solution. The reactions in the system are described by the general equations (3)–(6). In the three-component CHC–ZHC–talyum system,[230,232] zinc leads to stabilisation of the copper-containing phases and to more uniform distribution of the latter in the catalyst. The two components (ZnO and CuO) are mutually dispersed. Zinc oxide, on the one hand, stabilises copper, and on the other hand competes with it for calcium aluminate, with which they react according to Eqns. (3) and (4). In the two-component CHC–ZHC system, a chemical reaction giving a mixed hydroxide carbonate of Cu and Zn also takes place.[230,232,235] Thermal decomposition gives non-equilibrium solid solutions of Cu^{2+} in ZnO and of Zn^{2+} in CuO; electronic diffuse reflectance spectroscopy (EDRS) detected clusters or associates $(CuO)_x$. In the reduced specimens, an appreciable proportion of the copper is present not as crystallised Cu^0, and the surface of the copper-containing component is increased. Electron microscopy[28] showed that in the $CuO-CaAl_2O_4$ system the disordered copper phase has a globular structure; the introduction of ZnO leads to the formation of a copper phase with a more stable block structure. The thermal decomposition products of copper hydroxoaluminate, namely CuO, the $CuO-Al_2O_3$ solid solution, and then the spinel $CuAl_2O_4$, have a high degree of dispersion, which is preserved up to 600–700 °C.[236,237] A study of the thermal-vacuum electrical conductivity curves.[101,238] established that copper oxide reacts less strongly with the surface of the cements, compared with zinc oxide, and copper has a high surface mobility. A similar study of the CuO–ZnO system[239] detected isolated copper ions and $(CuO)_x$ clusters on the surface, both stabilised by ZnO. In a reducing medium, the copper-cement and nickel-cement systems show an unusual effect of low-temperature decomposition of $CaCO_3$,[125,126] which should lead to changes in the mechanical strength and surface properties of the specimen.

The conversion of CO by water vapour. The conversion of carbon monoxide on highly active copper catalysts at low temperatures makes it possible to decrease sharply the residual concentration of CO and to increase the H_2 concentration. Copper-containing catalysts on a cement base have been used for this purpose.[218,240–244] The NTM catalyst has a high activity at increased pressures.[218] The NTK-10 catalyst subjected to additional treatment[240] has a mechanical strength up to 600–800 kg cm^{-2}, withstands superheating to 300–350 °C, and gives a residual concentration of CO in the converted gas at 200–220 °C close to the equilibrium value. The increase in the strength and degree of compaction of the NTK-10 catalyst at the pressing stage is due to the breakdown of pores with dimensions >300 Å; decrease in the proportion of pores with a radius of 100–200 Å is accompanied by a decrease in the activity.[244] The use of $(NH_4)_2CO_3$ as pore-forming agent in copper-cement contact catalysts alters the porous structure and lowers the activity of the catalyst; this is due to the formation of copper–ammonia–carbonate complexes, which provide a source of copper with an increased ability to undergo recrystallisation.[245] Moist-air and hydrothermal treatment leads to an increase in strength, making it possible to use cement additives to restore the strength of the catalyst and enable it to be used again.[246] The highest activity is shown by catalysts for which the formation of the active phase involves the formation of copper hydroxoaluminate.[65,232,236,237] As finely dispersed CuO separates from the latter (with increase in temperature to 600 °C), the activity increases continuously, after which it decreases sharply as a result of the sintering of copper. For the same reason, the most active contact catalysts are those whose formation involves the reaction of CHC and talyum in the first stage, and the introduction of ZHC in the second:[232] this gives the maximum quantities of copper hydroxoaluminate. In $CuO-Al_2O_3$ and CuO–ZnO solid solutions, copper is converted into an active state ensuring the conversion of CO.[232,235–237]

The mechanism of the low-temperature conversion of CO by water vapour on NTK-10 copper–zinc cement catalysts has been studied.[247–250] The activity of the catalyst is related to its ability to adsorb CO in larger quantities, and H_2O and CO_2 in smaller quantities, on the non-uniform surface.[247] The reaction involves the formation of formate ion by a combined mechanism.[248] The formate complex is produced from CO_{ads} and OH_{ads}; the latter are produced by the dissociative adsorption of H_2O.[249] The temperature of the dissociative adsorption of water provides a criterion of the activity of copper-containing contact catalysts.[250] According to XPES and XAES data,[251] the active species is copper in the Cu^+ state; the zinc maintains copper in this state. A kinetic model of the reaction has been proposed, and the nature of the surface centres responsible for the reaction has been established.[252–254] The limiting stage is the surface reaction of the formate ion with the adsorbed hydroxyl group.

Synthesis of methanol. A large proportion of copper-containing catalysts for the conversion of CO are also active in the synthesis of CH_3OH. This applies to the copper–zinc cement contact catalyst.[218,233] In the synthesis of methanol, as in the conversion of CO, a high activity is shown by contact catalysts containing MHA.[230] A copper–zinc contact catalyst containing hydraulic cement is extremely effective.[255] Cements are also used in other catalysts for the synthesis of CH_3OH at a low pressure.[256]

Decomposition of methanol. Copper–zinc cement catalysts are effective in the decomposition of CH_3OH to CO and H_2.[257] Methyl formate can be obtained by dehydrogenating CH_3OH in the gas phase on a copper-cement catalyst at 150–300 °C.[258,259] The catalyst for the conversion of aqueous CH_3OH by water vapour at 300–600 °C contains group VIII metals, TiO_2, CeO_2, and a Ca aluminate cement.[260]

X. Catalysts for the hydrogenation of oxygen

In various branches of the national economy there is a demand for highly pure gases, in particular gases free from O_2. Gases free from oxygen are required for the hydrogenation of the products of organic synthesis, for example in the production of caprolactam, the hydrogenation of benzene, and the selective and complete hydrogenation of organic compounds. Inert gases free from O_2 are required in chemistry, metallurgy, and other fields. Analysis of data on the purification of technical gases from O_2 [261] showed that the most effective industrial catalysts are Pt, Pd, Cu, and Ni contact catalysts on carriers. The disadvantages of Pt and Pd contact catalysts are their high cost, scarcity, and low mechanical strength. An effective catalyst proposed for the hydrogenation of O_2 contains Ni, Cu, Al_2O_3, $CaCO_3$, and $CaAl_4O_7$;[262-268] this catalyst can operate without breakdown (mechanical strength 300–400 kg cm^{-2}) at temperatures of 100–700 °C and pressures up to 300 atm; the residual concentration of O_2 in Ar is ~0.0007 vol.%. Catalysts for purifying Ar, N_2, and H_2 [263] are obtained by mixing the hydroxide carbonates of Ni (NHC) and Cu (CHC) with talyum in the presence of aqueous NH_4OH solution. The catalyst ensures the removal of oxygen from the gas at oxygen concentrations down to 3.0–3.5% vol. O_2 (this is accompanied by an increase in temperature to 750–800 °C), indicating its high thermal stability and activity. The properties of talyum influence the production of the copper–nickel–aluminium–calcium contact catalyst.[264] Two reduction temperature ranges are observed (300 °C and 540 °C). After high-temperature reduction, the highest activity is shown by the catalyst with the lowest degree of reaction between the components; this may be brought about, for example, by slight preliminary subdivision of the talyum. On the other hand, the catalyst in which the extent of the reaction between the components and the concentrations of Ni and Cu hydroxoaluminates are fairly high shows the highest activity after high-temperature reduction. The possibility of replacing the industrial Pd catalyst AP-1 by the thermally stable and mechanically strong nickel–copper contact catalyst NKO-2 has been examined. Unlike the industrial nickel–chromium catalyst, the NKO-2 catalyst, after being swept with air, is not deactivated and shows no change in its basic characteristics.[265-267] Mixed Ni and Cu hydroxoaluminates provide the starting material for the formation of nickel–copper solid solutions which ensure stability of the active component of the catalysts to the effect of high temperatures and an oxidising medium.[268] The similarity in the reactivities of copper and nickel hydroxoaluminates leads to competition between them in the reaction with talyum. Copper hydroxoaluminate is more reactive.[269] In the NiO–CuO system, a solid solution based on CuO was detected on the surface; the probability of formation of this solid solution increases with increase in the copper concentration and the temperature of treatment.[270]

XI. Catalysts of the Fischer–Tropsch synthesis

Promising methods for the utilisation of coal and natural gas are provided by their conversion into synthesis gas with the subsequent production of hydrocarbons. Aluminium–calcium cements have been used to develop mechanically strong and thermally stable Co and Ni catalysts containing promoting additive (CuO, MgO) for carrying out reactions involving synthesis gas.[271-275] Their selectivity can be altered by varying the composition and conditions of preliminary treatment with hydrogen. Promotion by MgO leads to an increase in the polymerising properties, and modification by copper oxide makes it possible to restrict the growth of the carbon chain to 5–10 carbon atoms. Increase in pressure to 0.82 MPa led to an increase in the yield of liquid hydrocarbons and to the appearance in the products of hydrocarbons with a high melting point (synthetic ceresine).

A distinguishing feature of the mechanism of the production of cobalt–aluminium–calcium contact catalysts, as in the case of other aluminium–calcium catalysts, is the reaction of the components (CA and CA_2) with Co hydroxide carbonate (CoHC), which gives a carrier with a highly developed surface and an active component distributed on the surface. The catalysts show maximum selectivity in the synthesis of liquid hydrocarbons at a degree of reduction of the metal of 65–84%, which requires high-temperature treatment with hydrogen (550 °C).[29] One of the precursors of the catalytically active phase is Co hydroxoaluminate (CoHA),[274,275] which is reduced at 550–650 °C. Modification of the Co catalysts by CuO by the introduction of Cu hydroxide carbonate makes it possible to lower sharply the temperature of the reductive activation of the contact catalysts by 100–150 K and to increase the yield of liquid C_4–C_{10} hydrocarbons.[30,272,276] In the production of the Co–Cu catalysts, a multi-phase system with a highly developed surface (S_{sp} = 170 m^2 g^{-1}) is formed; both components influence the production of the inter-phase boundary.[30] A study of the thermal-vacuum electrical conductivity curves[276] established that CuO forms a solid solution in Co_3O_4, that is Cu cobaltite with variable composition and the spinel structure $Cu_xCo_{3-x}O_4$ ($0 < x < 1$) is produced, and is detected both in the bulk and on the surface. The carrier facilitates the reaction between the oxides and stabilises the surface cobaltite, which is detected even at a CuO concentration of 5% and a temperature of 200 °C. Copper oxide tends to concentrate on the surface of the particles, so that the surface cobaltite is richer in copper than the bulk cobaltite. Cobalt- and nickel-cement contact catalysts containing promoters are regarded as promising catalysts for syntheses based on CO and H_2.[277]

XII. Cement-containing contact catalysts with an acid–base action

The presence of varied acid–base centres in cement-containing catalysts[17,52,61-65,70] strongly suggests that these contact catalysts, in particular the aluminium–calcium catalysts, may be active in the isomerisation of hydrocarbons and the transformation of alcohols even without the introduction of any other elements. The dehydration and dehydrogenation of isopropyl alcohol take place intensively on calcium aluminates with a highly developed surface (galyumins).[52,62,65] The dehydration of the alcohol takes place on a pair of acid–base centres by a two-centre mechanism with the participation of the β-CH-groups of the reagent, and the dehydrogenation takes place on basic centres with the participation of α-CH-groups. The dehydration of α-acetylenic carbinols (prop-2-ynyl alcohol, dimethylethynyl carbinol) [278] also takes place on calcium aluminates by a two-centre mechanism with the participation of acid–base centres. The splitting of α-acetylenic carbinols to give acetylene is an indication of the presence of basic centres. The activity of the catalyst in the splitting reaction increases with increase in the ratio CaO/Al_2O_3. A decrease in the CaO concentration or blocking of the basic centres by the adsorption of an acid intensifies the dehydration of the alcohol. Galyumins

based on aluminium–calcium cements are effective catalysts of the reverse isomerisation of methylacetylene to allene.[279–285] The catalytic isomerisation of methylacetylene provides an accessible method for increasing the supply of allene on an industrial scale. Products based on allene are widely used in various branches of the national economy (dyes, leather, monomers, adhesives, medicines, etc.).[285] The reversible monomolecular isomerisation is described by a first-order equation.[279,282] The maximum value of the specific reaction rate constant is achieved at a definite ratio of the acidic and basic centres in the galyumins; the reaction rate is decreased by both acids (phenol) and bases (pyridine).[279–282] Effective catalytic methods have been developed for obtaining an equilibrium mixture of allene and methylacetylene from pyrolysis gases (methylacetylenic fraction).[283,284]

XIII. Catalytic systems for various organic and inorganic processes

The range of application of high-alumina cements, in particular the alkaline earth aluminates, in catalysis has been increasing continuously in recent years, covering the most varied processes involving the transformation of various nitrogen-, sulphur-, and carbon-containing compounds, from the preparation of the final products to the intensive purification of the effluent gases. The last process is acquiring increasing importance from the ecological viewpoint.

The formation and transformation of nitrogen-containing compounds. A method is known for obtaining oxides of nitrogen by the ionisation of air by a beam of electrons or γ-rays in the presence of calcium aluminates with a highly developed surface (galyumins).[286] The cobalt oxide (Co_3O_4)–calcium aluminate system is an effective and thermally stable catalyst for the oxidation of NH_3;[287–291] the yield of NO at 650 °C is 91.0%.[291] It is suggested[287,289] that $CaAl_2O_4$ actives Co_3O_4. A mechanically strong contact catalyst for the oxidation of NH_3, containing Ca, Al, Fe, and Cr oxides heated at 875–900 °C, has been described.[292] $CaAl_2O_4$ is added to the Fe-containing catalyst for the synthesis of NH_3 to increase its activity.[293] The use of calcium aluminates makes it possible to obtain Fe-containing catalyst blocks for NH_3 synthesis columns with an increased mechanical strength and good operational characteristics.[294] The decomposition of the carbonate component in these contact catalysts[295] takes place as a result of the catalytic action of the highly dispersed metal (Fe). Other metals have a similar effect.[125,126] Intensive enrichment of the surface of the BASF-56-10 industrial catalyst for the synthesis of NH_3 in Al and Ca oxides, which act together as surface promoters, has been described.[296]

Purification of effluent gases from CO. Platinum, rhodium, and ruthenium catalysts on a carrier containing cements and calcium aluminates can bring about the complete oxidation of CO even at room temperature.[297–304] The concentration of calcium aluminates is 35–90%.[299] Calcium aluminates containing 15–35% CaO are used.[300] In addition to Pt and Pd, the addition of compounds of metals of the iron group (Fe, Co, Ni) [305] and also Cu, Ag, Au, Mn, Cr, Sn, and Pb,[306] has been recommended; these contact catalysts are highly stable during use. MnO_2/calcium aluminates are also used to remove CO.[307] The presence of the calcium aluminates makes it possible to carry out the oxidation of CO on these contact catalysts in the presence of SO_2.[308] Fe and Cu oxides are effective promoters of catalysts based on MnO_x and calcium aluminates.[309] Aluminium–copper oxide catalysts with a ratio $Al_2O_3/CuO = 3:1$, modified by Ca, Sr, and Ba aluminates, can be used to oxidise CO at 150–450 °C.[310]

The purification of waste gases. The MnO_2–calcium aluminate catalytic system, which has a fairly high thermal stability, is used to purify spent gases, including exhaust gases, from CO and hydrocarbons.[311–315] Ca silicate and Portland cement can be used as the cement component.[314] Active components of the catalyst, in addition to Mn, are the oxides of Ni, Co, Cu, Fe, and Cr;[316–322] Ba or Sr aluminates are also added in addition to calcium aluminates.[317] The cement component of the catalyst increases its activity and thermal stability.[317] A cement-containing composition has a wide spectrum of action and makes it possible to remove not only hydrocarbons and CO, but also SO_2 and NO.[318,320] Catalysts including metals of the Pt group (Pt, Pd), and also activated carbon and calcium aluminates, have been described.[323–325] A contact catalyst consisting of spinel $M^{2+}M_2^{3+}O_4$ (M^{2+} = Mn, Fe, Co, Ni, Cu, Zn, Ba; M^{3+} = Fe, Al), calcium aluminates, and metal oxides active in oxidation has a high mechanical strength, porosity, and thermal stability;[326] it can be used to oxidise CO, hydrocarbons, SO_2, oxides of nitrogen, aliphatic acids, aldehydes, amines, and other compounds formed in the preparation of foodstuffs. An effective carrier for a catalyst for purifying effluent gases contains Al_2O_3 with added calcium aluminates.[327] An active copper–nickel–aluminium–calcium catalyst, not containing Mn or platinum metals, for purifying exhaust gases has been described.[328]

The catalytic combustion of organic compounds. Catalytic combustion processes are accompanied by strong thermal effects with an increase in temperature, creating severe operational conditions which lead to sintering and the loss of activity by the catalyst. The high melting points of Ca, Sr, and Ba aluminates makes them a suitable base for the production of thermally stable and highly active contact catalysts for catalytic combustion.[74,75,329,330] The sintering of γ-Al_2O_3 is suppressed sharply by adding Ca, Sr, and Ba oxides, capable of forming aluminate structures; a $CoO–BaO–Al_2O_3$ catalyst which has a highly developed surface due to the formation of $BaO.6Al_2O_3$ and which has a high activity in the combustion of CH_4 has been described.[74,75] The dispersion of Mn cations in a Ba aluminate matrix gave a contact catalyst with the composition $BaMnAl_{11}O_x$, whose activity is appreciably greater than that of familiar combustion catalysts such as Pt/Al_2O_3 and $LaCoO_3$.[330]

The partial oxidation of carbon-containing molecules. A highly pure composition containing Al_2O_3 and added barium aluminates, with a low S_{sp} and high mechanical strength, is used in the production of a silver-containing catalyst for the oxidation of ethylene to ethylene oxide.[76] A catalyst consisting of NiO, Al_2O_3, and calcium aluminates is used for the partial oxidation of hydrocarbons.[331] $CaAl_2O_4$ has been proposed as a carrier for a catalyst for the oxidation of C_3H_6 and $(CH_3)_2C=CH_2$ to unsaturated aldehydes and acids.[332] The possible oxidative transformation of CH_3OH to CH_2O over Mo, V, and W oxides deposited on talyum ($CaAl_2O_4$ + $CaAl_4O_7$) has been studied.[333–335] The oxidative dehydrogenation of methanol is accompanied by its oxidation to CO and CO_2, and also by dehydration to $(CH_3)_2O$.

The hydrogenation, dehydrogenation, hydrogenolysis, and alkylation of carbon-containing compounds. The selective dehydrogenation of alkylaromatic hydrocarbons to styrene and its derivatives is carried out on Fe–Cr catalysts containing calcium aluminates, Portland cements, or alumina cement.[336–341] The role of the cements is varied: they increase the selectivity, and act as a binding agent. The introduction of $CaAl_2O_4$ into copper–aluminium and copper–magnesium catalysts for the dehydrogenation of cyclohexanol increases the rigidity of their framework and leads to suppression of the dehydration, increasing the selectivity of the process.[342–344] Aluminium–calcium cement or calcium aluminates with an atomic ratio Ca/Al = 1/(4–10), subjected to thermal treatment at ~1000 °C, after the introduction of Pd are used for the selective hydrogenation of small quantities of more unsaturated compounds (C_2H_2) in the presence of less saturated compounds (C_2H_4).[345,346] The dehydrocyclisation of n-hexane can be carried out on aluminium–chromium–calcium catalysts.[347] The addition of alkaline earth metal oxides, preferably CaO (25%), increases the lifetime, activity, and selectivity of a 0.1–5% Pd/Al_2O_3 catalyst in a single-stage industrial method for obtaining highly pure cyclohexanone by the hydrogenation of phenol at 130–160 °C.[348] The best carrier for the catalyst for the synthesis of stilbene and its derivatives by the oxidative dehydrogenation of toluene and its derivatives in the vapour phase is calcium aluminate or Alcoa-CA-25 aluminate cement.[349–357] During mixing and high-temperature treatment (up to 800 °C), the carrier reacts with the active component; the basic character of the carrier prevents coke formation on the contact catalyst.

The catalytic systems $Ni–Al_2O_3–CaO$, $Ni–Al_2O_3–SrO$, and $Ni–Al_2O_3–BaO$ can be used for the liquid-phase hydrogenolysis of glucose to obtain glycerol and glycols.[358–362] The basic properties of the cement have a positive influence on the process, which takes place preferentially in a medium with a high pH. Since the medium is highly corrosive, it is appropriate to carry out carbonisation of the surface to increase the stability of the contact catalyst. CaO/Al_2O_3, $(CaO + SrO)/Al_2O_3$, and $(CaO + NiO)/Al_2O_3$ compositions have been patented[363] as catalysts for obtaining C_3H_6 from C_4H_{10} at 350–700 °C; the conversion of C_4H_{10} reaches 91%, the yield of C_3H_6 50%, and the ratio C_3H_6/C_2H_4 = 2.7. A catalyst for cracking high-boiling fractions with a large C/H ratio consists of calcium aluminates ($C_{12}A_7$, CA_6, CA, CA_2) and Ba and Sr aluminates, sintered at 1300–1500 °C, with the addition of 0.1–3% of activators (K vanadates).[364] The alkylation of cyclopentadiene and its derivatives by lower alkanols (C_4) is carried out in the presence of basic heterogeneous catalysts, for example a mixture of $Ca(OH)_2$ and Al_2O_3 heated at 1000 °C and treated with water.[365]

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The authors have tried to analyse the principal trends and the most important directions of development of heterogeneous catalysis using cement-containing contact catalysts.

There are grounds for hoping that cement-containing catalysts can be used for the most varied low- and high-temperature processes in organic and inorganic technology. A new research field has now been established, associated with the preparation of oxide and metal oxide mixed cement-containing catalysts. Work is beginning to be developed on the production of deposited cement-containing catalysts. The physicochemical principles of the synthesis of cement-containing catalysts, carriers, and adsorbents for use in gas-phase and liquid-phase processes have been developed, and the regular features of the increase in the strength of their structure at the stages of tablet formation and hydration hardening have been studied. For the preparation of these catalysts, in addition to the already fairly familiar Ca, Sr, and Ba aluminates and high-alumina cements of the talyum type (TU-6-03-339-78), successful use is now beginning to be made of aluminothermal cements such as VTs-70, VTs-75 (TU-21-20-60-84), and also the specially developed high-alumina cement which has been called talyumin (TU-113-03-31-50-88). The physicochemical principles of the preparation of new highly pure high alumina cements have been developed.[9,32]

Cement-containing catalysts are used in more than 100 factories only in the Soviet Union. More than 200 patents covering cement-based catalysts have been published. Assemblies are being developed for the production of cement-containing catalysts by a universal and flexible technology. The use of cement-containing catalysts should help to solve problems of saving raw materials and energy, effectively converting carbon-containing raw material into required end products, protecting the environment, and establishing waste-free industries.

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Progress in the synthesis of grafted materials using radiation graft polymerisation

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ABSTRACT. The current state of research into graft polymerisation processes that are initiated by ionising radiation is examined. Particular attention is given to new radiation grafting methods, such as low-temperature graft post-polymerisation, grafting with plasma chemical initiation, grafting in the presence of complexing agents, and grafting of metal-containing monomers. The mechanism of the radiation graft polymerisation process is also discussed.

The bibliography includes 188 references.

Contents

I.	Introduction	469
II.	Direct grafting	469
III.	Low-temperature post-radiation graft polymerisation	471
IV.	Plasma-initiated grafting	472
V.	Effect of matrix structure on post-radiation grafting	472
VI.	Complexation as a method of controlling graft post-polymerisation	473
VII.	The peroxide method and grafting of metal-containing monomers	474
VIII.	The mechanism of radiation graft polymerisation	474

I. Introduction

Graft polymerisation is currently one of the most promising methods for obtaining modified polymer materials which combine different, and often contrasting, properties. There is an extensive literature, including a number of monographs and reviews,[1–24] which is devoted to different aspects of graft polymerisation — the procedural method, a study of its basic principles, its kinetics and mechanism, the structure and physicochemical properties of graft polymer materials, and problems in carrying out the processes on a pilot and industrial scale.

Amongst the many methods for obtaining graft copolymers, radiation graft polymerisation plays an important role. The radiation method for initiation of grafting is the most versatile method, and it can be used to carry out the process in virtually any system of matrix–grafted monomer. The radiochemical initiation of graft polymerisation has a number of advantages over a material method.[25]

Radiation graft polymerisation has up to the present time evolved as an independent branch of science with its own methodology and wide range of problems that can be resolved by it relating to the overall task of obtaining materials with a given set of production and operating properties. Considerable progress has been made in the practical realisation of processes based on radiation graft polymerisation. Thus, radiation finishing of textile materials is widely used.[15,16,21,22] Radiation grafting is used to obtain biocompatible polymer materials for medical application and materials for the immobilisation of biologically active compounds and samples,[26–44] adhesive polymers,[45–54] ion-exchange materials,[55–63] and supported catalysts and other materials.[24]

In the present review the most recent advances in the development of methods for obtaining radiation grafted polymer materials and a study of the mechanism of radiation graft polymerisation are examined.

II. Direct grafting

The main methods of radiation graft polymerisation had already been developed by the start of the 1960s and are covered in sufficient detail in review articles.[1–4,6,8,10–12,14–17,19,21,22,24] There are four main methods of radiation grafting: 1) the direct method, i.e., direct irradiation of the system: polymer being modified–monomer being grafted; 2) post-polymerisation, i.e., initial irradiation of the polymer in the absence of air followed by contact of the monomer with the irradiated polymer; 3) the peroxide method, i.e., initial irradiation of the polymer in an atmosphere of air or oxygen followed by treatment of the irradiated polymer with the monomer under conditions where the peroxides and hydroperoxides formed by irradiation decompose; 4) cross-linking of polymer mixtures. The last of these methods has not been developed to any significant extent. In the development of the first three methods, however, there have been a number of new results in recent years that have considerable significance for synthetic radiation chemistry.

The direct method has become the most widely used method for radiation graft polymerisation. Most frequently the polymer is in contact during irradiation with an excess of monomer, which can be used in liquid form (including in solution) or gaseous form. Sometimes use is made of the initial impregnation method, in which the polymer is first impregnated with the monomer and then irradiated. The method is non-stationary since there is no additional supply of monomer when it is consumed. The advantage of the direct method is that it occurs in a single stage, and the main disadvantage is the possibility of homopolymerisation of the monomer used for grafting occurring at the same time as a side-reaction; this is particularly significant in liquid-phase processes.

The methods for suppressing homopolymerisation during direct grafting have been examined in detail.[24]

One of these methods involves the introduction of transition metal ions into the system. This method is used particularly often in liquid-phase grafting. Recently a number of studies have been published on the kinetics of direct radiation liquid-phase grafting in a system of such practical importance as polyethylene (PE)–acrylic acid (AA)–water–Mohr's salt.[64–66] By comparing the effect of the dose rate, concentrations of monomer and ferrous ions on the kinetics of graft polymerisation of AA on to PE and the kinetics of homopolymerisation of AA, it was possible to optimise the conditions for grafting of AA on to PE in an aqueous solution of monomer.[66]

There is a certain interest in introducing organic compounds that are polymerisation inhibitors into the system. By using the difference in the ability of inhibitor and monomer molecules to diffuse to the active sites that initiate polymerisation in the polymer matrix, it is possible not only to suppress the unwanted homopolymerisation process in the external solution but also to control the distribution of graft polymer with respect to the thickness of modified material.[67] The chemical addition of components to the chains of graft polymer is also possible, as a result of which a substantial increase in the stability of the material towards thermal stability and oxidation and also deformation strength properties is achieved.[68–70]

Out of the different variants of the direct method of radiation graft polymerisation, it is gas-phase grafting that has been successfully developed.[15,16,21,22] This method involves the irradiation of different solid supports, including mineral supports,[15,16,22,71] in the presence of monomers that are in the gas phase or in the form of unsaturated vapour. The energy of irradiation in this case is absorbed almost solely by the solid support, as a result of which active sites initiating polymerisation are essentially formed only in it. Consequently, homopolymerisation in the gas phase is almost completely suppressed and, moreover, there is the possibility of grafting in those systems which are characterised by a low radiochemical yield of active sites in the support compared to their yield in the monomer. For graft polymers obtained by gas-phase graft polymerisation, a layered macroheterogeneous structure with a distinct boundary between the grafted and ungrafted layers is typical as is the formation of ordered (crystalline and oriented) structures of the graft polymer when using polymers in an oriented state as supports.[72]

In studying the structure of radiation grafted polymer materials obtained by the direct method, attention has until recently mainly been focussed on the macrodistribution of the graft polymer and the characteristics of ordering of the macromolecules. Experimental methods for analysing non-uniformity in the distribution of a graft polymer on the surface and width of a modified polymer material have been developed further. Thus, for studying the surface of grafted polymer films and fibres, the use of a radioactive indicator method has been proposed[77] along with the traditional methods of optical[73–75] and electron[51,76] microscopy. According to the former method a radioactive label is introduced into grafted chains, after which an image is obtained on a photographic plate, characterising the irregularity of distribution of the graft polymer on the surface of the sample. For this purpose it has been proposed to utilise the different capacity of the chains of polymer matrix and grafted polymer to undergo radiothermoluminescence.[78] In order to study irregularity in the distribution of a grafted polymer along the cross-section of a modified sample, in addition to the known indirect methods that consist of an analysis of the dependence of the content of the grafted polymer on the thickness of the sample and changes in geometric dimensions on the material during grafting and the direct methods related to a study of lateral sections of grafted polymer materials, a method based on comparison of optical densities in IR transition and multiply attenuated internal reflection spectra has been put forward.[79] In addition to inteferrometry,[80] microprobe X-ray spectroscopic analysis[63,81,82] has started to be widely used for the analysis of sections of graft polymer materials. It was possible, in particular, to use this method to establish the broken, step-like nature of the edge of the graft in graft copolymers of PE with AA obtained by direct irradiation in an aqueous solution of AA in the presence of Mohr's salt.[82]

There has also been further development of theoretical methods for analysing the irregularity of distribution of a graft polymer along the cross-section of radiation grafted polymer materials; these are based on the equations of diffusion kinetics.[16,83,84] In one study,[85] in order to determine the characteristic parameter, α, which can be used to determine the concentration distribution profile of a graft polymer along the cross-section of a sample, a transcendental equation has been obtained and solved, which contains only experimentally measured parameters of radiation graft polymerisation—the rate of grafting, the degree of equilibrium sorption of the monomer, the diffusion coefficient of the monomer in the polymer, and also the thickness of the modified material. Calculation of the width of a grafted layer from the value of the parameter α has been improved.[86]

In a study of the radiation grafted films and fibres of PE–polyacrylonitrile and chlorinated polyvinyl chloride–polyacrylonitrile synthesised by direct irradiation in monomer vapour with high dose rates, experimental confirmation has been obtained for the existence of "cut-off" layers on the surface of grafted materials,[87] whose possible occurrence had been considered previously.[15,16] Comparison of the strength and vapour permeability of samples with a "cut-off" layer, obtained at a high dose rate, and samples obtained at a low dose rate and not containing a "cut-off" layer showed that in the first case a considerable change in the properties of the material was achieved even with a small content of grafted polymer whereas in the second case there were only substantial changes in the properties for high degrees of grafting.[87]

In recent times, starting with the studies of Kurilenko et al.,[88–90] for radiation grafted polymer materials there has been considerable development of ideas about the heterogeneous nature of graft polymerisation and the microdistribution of components in graft copolymers, as proposed by Kargin and Platé in the 1950s. In addition to low-angle X-ray dispersion and electron microscopy,[23,75,87–90] low-angle neutron has been successfully used to obtain distribution curves of the dimensions of the particles of the microphase of a graft polymer for an analysis of the microheterogeneous structure of radiation grafted polymer materials.[91,92] Ideas about the microheterogeneous structure of radiation grafted polymer materials and the effect of the particles of the microphase of a grafted polymer on the molecular mobility and interchain interaction in amorphous microregions of a modified polymer have been used to analyse the causes of the change in thermal and deformation strength properties of polymer materials from radiation grafting.[23]

Out of the studies on direct radiation grafting which have undergone considerable development, mention should be made of radiation grafting on to latex particles from emulsions.[24] Radiation emulsion polymerisation is one of the most promising developments

in radiochemical technology.[93] It combines the advantages of emulsion polymerisation and radiation initiation. Several examples of radiation emulsion graft polymerisation are reported in the literature.[94-105] Thus, the radiation emulsion grafting of styrene, vinyl acetate, butyl methacrylate, and methyl methacrylate (MMA) on to lattices of polyvinyl acetate, polybutyl acrylate, and polymethyl methacrylate (PMMA) occurs in high yield (up to 80%).[94] The radiation grafting of styrene, vinyl acetate, ethyl acrylate, and MMA on to polytetrafluoroethylene (PTFE) in a latex has been studied.[95] Grafting did not occur at all with chemical initiation whereas with radiation grafting the quantity of graft polymer reached 6–8% of the weight of PTFE. Grafting by irradiation of lattices in the systems polyvinyl acetate–acrylonitrile (AN) and polyethyl acrylate–MMA was also studied.[95] The content of graft copolymer in the final product reached 40–50%. The radiation graft polymerisation of MMA on to polybutyl acrylate in an emulsion has been established,[96] and the radiation graft polymerisation of styrene in a polybutadiene latex has been studied.[97-99] The results were compared with those obtained by chemical initiation under the same conditions. No significant difference in the degree of grafting was observed for both methods of initiation; this was attributed to the ease of transfer of a growing polystyrene chain to polybutadiene with removal of a hydrogen atom at a α-position relative to the double bond.[24] The resulting polymer radical is one of the main sites of grafting. Therefore, the additional formation of polymer radicals on polybutadiene during irradiation does not make a significant contribution to the overall degree of grafting.

The radiation grafting of styrene and AN on to a polybutyl acrylate latex has been reported.[100] The quantities of graft copolymer amount to double-figure percentages, the yield of graft increasing as the ratio of water to polymer in the initial latex increases, which is related to the preferential participation of the radiolysis products of water in graft polymerisation rather than homopolymerisation. The process of obtaining an atmospherically stable, high-impact plastic which is based on the radiation grafting of a styrene copolymer and AN on to a rubber latex has been reported.[101-105] The plastic obtained has physicomechanical properties which are not inferior to ternary copolymers of AN, butadiene, and styrene (ABS plastic) and are frequently superior to them in terms of atmosphere stability. This extends their range of application.

The combined literature data provide an indication of the high efficiency of radiation graft emulsion polymerisation compared to other forms of radiation grafting due to the more extensive surface of the matrix. In materials obtained by radiation emulsion graft polymerisation there is a sufficiently uniform distribution of macromolecules of a different chemical nature throughout the bulk of the sample.

The advantages of the radiation method for initiation in emulsion graft polymerisation are particularly obvious in grafting on to polymers that do not tend to undergo chain-transfer reactions. We should note that there is virtually no information about the physicochemical properties of polymer materials obtained by radiation emulsion graft polymerisation.

III. Low-temperature post-radiation graft polymerisation

Low-temperature post-radiation grafting with devitrification of the polymer matrix is one of the relatively new methods used to carry out graft polymerisation. This method has been discussed in two reviews.[106,107] and in a study published later.[108] In essence the method involves the introduction of a monomer into the polymer being modified by sorption from a liquid or gas phase, the system is cooled to a temperature below the glass-transition temperature of the polymer, exposed to ionising radiation at this temperature, and then devitrified. Direct grafting of a monomer in solution does not occur in a vitrified polymer. Radiation graft post-polymerisation is only achieved by devitrification of the polymer matrix, and it occurs at a high rate with virtually no formation of homopolymer. Acceleration of grafting at temperatures corresponding to transition of the matrix from a vitreous form to a hyperelastic form had previously been recorded.[109,110] A significant shortcoming of these studies was the use of the traditional gravimetric method for determining the yield of polymer, the yield of graft polymer being determined at room temperature and not at the temperature corresponding to the maximum rate of graft polymerisation. For low-temperature processes the yield of graft polymer was actually determined after decomposition of the vitreous matrix. For quantitative kinetic studies necessary for an understanding of the processes that occur during devitrification of the matrix, methods were needed which would allow a process to be monitored directly as it occurred and not after its completion and decomposition of the surrounding matrix. It was also necessary to analyse in each particular case the two-component system "monomer–vitrifying matrix", to determine the limits of mutual solubility at the glass-transition temperatures of the system, and finally the temperature itself in the region of vitrification. All these methodological problems were successfully resolved by the use of a calorimetric technique.[107]

It was shown that most monomers introduced into a polymer matrix by sorption are preserved in the form of a solution in the pores of the matrix on freezing. A characteristic crystalline phase of monomer is formed when it is in excess, but this occurs in far from every case for all of the monomers. In the devitrification of a polymer mtrix an intense evolution of heat occurred, related to the process of polymerisation, which in a number of cases was confirmed by IR spectra to be grafted in nature.[108,111-115] Studies were also carried out on systems such as polyisobutylene–AN, polyisobutylene–divinylbenzene, polyisobutylene–methyl acrylate, polyisobutylene–MMA,[111] polyisobutylene–tetrafluoroethylene (TFE),[108] PE–TFE,[112] ethylene–propylene rubber (EPR)–TFE,[108,113-115] polydimethylsiloxane–AN, polydimethylsiloxane–MMA, polydimethylsiloxane–methyl acrylate, polydimethylsiloxane–vinyl acetate,[114] polydimethylsiloxane–TFE,[108,114,115] polydimethylsiloxane–styrene, polydimethylsiloxane–butadiene, polydimethylsiloxane–vinyl fluoride,[114] polydimethylvinylsiloxane–TFE, polydimethylphenylmethylvinylsiloxane–TFE, polydimethylmethylphenylsiloxane–TFE, polystyrene–TFE, PMMA–TFE, fluororubber SF-26–TFE, polybutadiene–TFA, butyl rubber–TFE, polyvinyl chloride–TFE.[108] In all systems, with the exception of polydimethylsiloxane–styrene, polydimethylsiloxane–butadiene, polydimethylsiloxane–vinyl fluoride, polymerisation of the introduced monomer occurred at about the temperatures corresponding to devitrification of the polymer matrix. High values of the yield graft of polymer were achieved in the rubber matrices, especially those of silicones. Graft polymerisation occurred

throughout the whole volume of the matrix and yielded materials with a uniform distribution of graft polymer along their cross-section.

The main advantage of low-temperature post-radiation graft polymerisation over other methods of radiation grafting lies in the possibility of obtaining graft copolymers with such readily polymerising and difficult to graft monomers as fluoroolefins, in particular, TFE. There is future potential in the low-temperature post-radiation grafting of TFE to by-products of the processing of PTFE, which would make it possible to obtain monolithic blocks of PTFE from the by-products, similar in properties to the initial polymer,[116,117] as is the low-temperature grafting of vinyl fluoride and vinylidene fluoride to by-products of the production of PTFE, PE, and polyvinyl chloride.[118–122]

The physicochemical properties of the materials obtained by low-temperature post-radiation graft polymerisation have been insufficiently studied. In one review[106] it was pointed out that graft copolymers with TFE have improved thermal and chemical stability and a lower coefficient of friction compared to the initial polymers. The improved heat stability of a graft polymer of PE with vinyl fluoride compared to the initial PE has also been recorded.[119] The properties of graft polymer materials obtained by low-temperature post-radiation grafting and their structures have not been studied in detail.

IV. Plasma-initiated grafting

Initiation of graft polymerisation with a non-equilibrium plasma from a gaseous discharge is regarded at the present time as a novel method of radiation graft polymerisation.[22] Although plasma-initiated graft polymerisation, as was mentioned by Tsetlin et al.,[22] can be achieved using the direct method, most of the published articles relate to plasma-initiated graft post-polymerisation.

The first studies on the effect of a high-frequency gas discharge plasma on solid organic compounds, including monomers in a vitrified state, were carried out at the beginning of the 1960s.[123] At that time the possibility of using radicals formed by discharge on the surface layer of a polymer for the synthesis of graft copolymers was suggested.[124] The preparation of graft copolymers of cellulose with ethyl acrylate by initiating the process with a corona discharge was reported.[125]

In recent years the processes which occur in PE on exposure to a non-equilibrium gas discharge plasma have been studied in detail,[126,127] and methods have been developed from this for plasma-initiated graft polymerisation of MMA, AA, methacrylic acid on to PE powder.[128,129] In essence the methods involve PE powders being evacuated, and then at a small residual pressure of oxygen (10–260 Pa) or in an atmosphere of an inert gas they undergo treatment with a high-frequency gas discharge plasma, after which the PE is again evacuated and brought into contact with monomer vapour, resulting in plasma-initiated post-polymerisation. It has been shown that neither a wide variation in pressure of the inert gas nor in specific power of discharge has an effect on the initial rate of grafting of MMA on to PE, which, however, depends on the time of treatment of PE in the plasma. Thus, for the first 3–5 min of treatment with the plasma, the rate of grafting of MMA on to PE increases substantially and then remains virtually unchanged, which is due to the attainment of a given limiting concentration of active sites or products initiating the reaction.[129] Plasma-initiated grafting of methacrylic acid on to PE occurs at a higher rate than grafting with AA.[128] Grafting of water-soluble monomers on to PE films, polypropylene (PP), and polyethylene terephthalate, treated with a high-frequency discharge plasma, from aqueous solutions of AA, 2-hydroxyethyl methacrylate, 2-dimethylaminoethyl methacrylate, vinylpyridine, acrylamide, and 2-acrylamide-2-methyl-1-propanesulphonic acid has been reported.[130] Comparison of the kinetics of plasma-initiated grafting of AA on to PE powder with γ-initiated graft post-polymerisation (Fig. 1) showed that a similarity of the kinetic curves for formation of graft polyacrylic acid (PAA) is achieved at a dose of 40 kGy.[23,128] Consequently, in certain cases plasma-initiated grafting in terms of both energy and process equipment design may be preferable than that initiated by γ-irradiation or accelerated electrons.

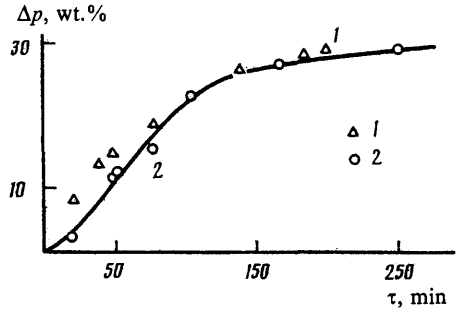


Figure 1. Dependence of the degree of grafting (ΔP) of AA on to PE on the time of the process for plasma-initiated post-polymerisation after initial treatment of PE for 10 min in a helium plasma at a pressure of 9.3×10^2 (*1*) and for γ-initiated post-polymerisation with an irradiation dose of 40 kGy (*2*); temperature of grafting was 323 K.[128]

A characteristic of plasma-initiated graft polymerisation is the occurrence of the process on the surface layer of the modified material with thickness of several μm, where the active sites that initiate grafting are primarily located. The nature of these sites and their relative efficiency in initiating the process of graft polymerisation is not yet completely clear. It has been noted[24] that plasma-initiated grafting may be a convenient method for modifying the surface properties of polymer materials, but these properties have also been sufficiently studied. There is future potential in the use of PE powder grafted by plasma chemical initiation for immobilisation of supported polymerisation catalysts[128] and PE films for adsorption of metal ions.[130] The mechanical properties of films that are grafted by plasma chemical means have hardly been studied at all.

V. Effect of matrix structure on post-radiation grafting

A series of studies by Nikol'skii et al.[75,131–134] is concerned with the dependence of the rate of gas-phase graft post-polymerisation of vinyl monomers (mainly styrene) to polyolefins on the characteristics of their hypermolecular structure. The structure of PE and PP films was modified by changing the rate of cooling the polymer melt and also by annealing. The dependence of the radiochemical yield of the

radicals, stable at 77 K and quasi-stable at room temperature, was studied. The yield of radiation graft copolymer was studied in parallel. It was shown[131] that the radiochemical yield of the free radicals in low-density PE at 77 K did not depend on the rate of cooling the polymer melt when it was changed from 1.5 to 2000 K min^{-1} and constituted 3 sp/100 eV. The magnitude of the radiochemical yield of radicals that were quasi-stable at room temperature increased by 25–30% on reducing the rate of cooling from 2000 to 1.5 K min^{-1}. At the same time the yield of polystyrene and polyacrylonitrile, grafted on to PE by gas-phase graft post-polymerisation on alkyl radicals that were quasi-stable at room temperature and also by liquid-phase grafting on alkoxyl radicals formed by the thermal decomposition of hydroperoxide groups in PE irradiated in air, increased several times on reducing the rate of cooling by a factor of 10–100. Hence, reduction in the rate of cooling a PE film by a factor of 10–100 during its preparation makes it possible to reduce the dose necessary for grafting by a considerable amount.

Studies carried out with low- and high-density PE films obtained with rapid cooling (cooling rate 2000 K min^{-1}) and annealed for 7 h under vacuum at 313–393 K showed that the radiochemical yield of free radicals at 77 K, equal to 3 sp/100 eV for annealed films, increases on annealing by only 10–20% whereas the radiochemical yield of radicals that are quasi-stable at 295 K increases more markedly.[133] The yield of polystyrene grafted on to PE using gas-phase graft polymerisation increases to a greater degree than the yield of radicals that are quasi-stable at room temperature. A study of the structure of annealed films showed that as the temperature of annealing increases the density of polymer and its crystallinity increase. The initial rate of sorption of styrene increases on annealing by 20–30% while the maximum sorption, on the other hand, is slightly reduced. The increase in yield of graft polystyrene correlates with the increase in concentration of free radicals that are quasi-stable at room temperature.

Rapidly cooled low-density PE films were compared[132] with slowly cooled high-density PE films. The rapidly cooled (quenched) low-density PE films did not contain spherulites, but when they were annealed spherulites of diameter 6–9 μm appeared. At the same time the density and (X-ray) crystallinity of the polymer increased and there was a reduction in the adsorption of styrene. The slowly cooled high-density PE films had a spherulite structure with spherulites of average diameter 3–6 μm. On annealing the diameter of the spherulites increased to 15–20 μm. At the same time the density and crystallinity of the polymer increased. The radiochemical yield of free radicals at 77 K in all of the samples was 3 sp/100 eV. The concentration of radicals that were quasi-stable at room temperature in the slowly cooled high-density PE films was 2–3 times higher than in the rapidly cooled low-density PE films. Annealing led to an increase in concentration of these radicals, this being exhibited most distinctly for high-density PE. Gas-phase graft post-polymerisation of styrene on slowly cooled films on the whole occurred at a higher rate than on rapidly cooled films.

Similar characteristics of the effect of the rate of cooling and annealing temperature on the yield of graft polystyrene were determined in the system PP–styrene.[134] A spherulite structure formed in PP on slow cooling of the melt, and on rapid cooling a smectic structure occurred. Annealing led to an increase in crystallinity and a sharp increase in the yield of graft polystyrene, which was due to an increase in concentration of radicals that were quasi-stable at room temperature as well as an improvement in conditions for sorption and diffusion of the monomer.

It was also shown[132–134] that the dependence of the degree of grafting on the thickness of the initial polyolefin film is extremal in nature, the position of the maximum being determined by the conditions of crystallisation and the annealing of the sample and also by parameters of the grafting process such as reaction time and radiation dose. On the basis of the kinetic data, it was suggested[132–134] that the maximum in the dependence of the degree of grafting on the thickness of the sample corresponds to the start of a gradual change from "bulk" grafting, characterised by a comparatively uniform distribution of graft component, to "surface" grafting, where the graft polymer is localised in the layer of material near the surface.

VI. Complexation as a method of controlling graft polymerisation

Complexation which achieves stabilisation of the macroradicals growing during polymerisation is used to control radiation graft post-polymerisation processes.[135–138] Thus, the polymerisation of acrylic and methacrylic monomers in the presence of orthophosphoric acid occurs in apparently homogeneous solutions and after the incorporation of an initiation source.[139] The cause of the suppression of bimolecular termination is the cross-linking of the polymerisation system through the formation of macromolecular and radical associates that are stabilised by hydrogen bonding. By using radicals bound on to cellulose for initiation of polymerisation in the system H_3PO_4–acrylic or methacrylic monomer, it was possible to obtain graft copolymers.[135] We should mention that complexation has also been used in direct radiation grafting, making it possible to obtain graft copolymers with allyl monomers in good yield.[140] The γ-initiated graft post-polymerisation of MMA and methyl α-chloroacrylate on to cellophane film in the presence of H_3PO_4 has been studied in detail.[135] Irradiation of the film was carried out at 77 K with grafting at room temperature. Grafting did not occur in the absence of H_3PO_4. When the complexing agent was added, grafting occurred, and in the initial stages of the process a linear increase in the content of graft polymer and its molecular weight with time was observed when there was a constant number of graft chains. Consequently, in the presence of H_3PO_4 graft post-polymerisation of MMA to γ-irradiated cellulose occurred virtually without termination or chain transfer, so that it was possible to obtain by a "living" mechanism grafted block copolymers of cellulose–(graft)(MMA–block methyl α-chloroacrylate). Graft copolymers of cellulose triacetate with a regularly varying number and length of PMMA chains were synthesised by means of continuous irradiation post-polymerisation of MMA in the presence of H_3PO_4.[136] A characteristic of this system was the increase in the number of grafted chains with grafting, which Akrabov et al.[136] attributed to the progressive involvement in graft polymerisation of macroradicals of cellulose triacetate that accumulated during γ-irradiation. It was observed[135] that the materials obtained using continuous irradiation graft polymerisation are characterised by a uniform distribution of graft polymer along their cross-section. For graft copolymers of cellulose triacetate with PMMA synthesised in the presence of H_3PO_4, the thermodynamic properties of their solutions were studied.[141] The dependence of the physicochemical properties of graft copolymers of PE synthesised using material initiators on the length and frequency of the graft chains has previously been recorded.[142,143] Hence there would be considerable interest in research into the properties of graft copolymers obtained

by means of continuous irradiation polymerisation in the presence of a complexing agent; this could help to determine the dependence of the physicochemical properties of radiation grafted polymer materials on the parameters of their molecular structure.

VII. The peroxide method and grafting of metal-containing monomers

The peroxide method of radiation graft polymerisation has been widely used since the 1950s,[3] but its mechanism cannot yet be regarded as established conclusively. A series of studies relating to both the mechanism of grafting conventional monomers (AA, acrylamide) on to PE and an investigation of the features of graft polymerisation of metal-containing monomers on to PE is of prime importance for the development of research on radiation graft polymerisation using the peroxide method.[144,148,149,151–153]

The nature of the active sites that initate grafting using the peroxide method is still the subject of controversy. The results of experiments on the grafting of AA on to irradiated PE powder and on to the same powder after iodometric titration resulting in decomposition of the hydroperoxides have been compared.[144] In the latter case grafting did not occur at all, from which it was concluded that hydroperoxides had higher activity than dialkylperoxides in graft polymerisation.

Transition metal salts are used to accelerate graft polymerisation by the peroxide method. The addition of small quantities of these leads to a more efficient decomposition of the peroxides.[145–147] It was shown[148] that on increasing the concentration of cobalt palmitate from 0 to 0.8%, the initial rate of radiation grafting of AA on to irradiated PE powder in a solution of monomer in heptane increased by a factor of two. In contrast to the grafting of AA on to PE,[148] there was no detectable accelerating action of cobalt salts on the grafting of acrylamide on to PE. A possible reason for this phenomenon, in the opinion of Savost'yanov et al.,[149] could be the formation of complexes between the cobalt compounds and acrylamide.[150]

In a study of graft polymerisation of Co(II), Ni(II), and Cu(II) acrylates on to PE powder that had previously been irradiated in air, it was shown[152] that this process occurs at lower rates than grafting with AA. In the grafting of acrylamide complexes of Co(II), Ni(II), and Cu(II) [composition of the complex was $MX_2 \cdot 4AA$, where M = Cu(II), Ni(II), Cu(II), X = Cl or NO_3, AA = acrylamide) to PE powder that had previously been irradiated in air, homopolymerisation was completely suppressed and the initial rate of grafting and yield of graft polymer were similar to those values that were observed in grafting of pure acrylamide.[153] The only exception to this was the $CuCl_4 \cdot 4AA$ complex, which underwent virtually no grafting on to irradiated PE.

There is also virtually no grafting of allyl alcohol on to PE previously irradiated in air, whereas complex compounds of allyl alcohol with transition metal salts [particularly with $Co(NO_3)_2 \cdot 6H_2O$, $CoCl_2$, and $CoCl_2 \cdot 6H_2O$] are grafted at a high rate.[151]

Thus, by using metal-containing monomers in the modification of polymer materials by radiation graft polymerisation with the peroxide method, it is possible in certain cases to carry out the grafting of monomers that are usually grafted with difficulty. Metal-containing graft copolymers are of interest in the treatment of polymerisation catalysts.[128] Moreover, they could most probably be used as materials with increased heat stability by analogy with ionomers.[154] However, the physicochemical properties of materials obtained by extrusion of PE with graft metal-containing polymers have hardly been studied at all.

VIII. The mechanism of radiation graft polymerisation

In the 1970s there was considerable progress in studies relating to radiation graft polymerisation.[155–169] For a long time it was thought that radiation graft polymerisation at room temperature and higher temperatures occurred solely by a radical mechanism. Direct evidence for such a graft mechanism was obtained for certain systems. Thus, in a study of radiation gas-phase graft copolymerisation of AA and styrene on to PP fibres there was agreement between the values of the relative activities r_1 and r_2 obtained during radiation copolymerisation from the gas phase and the corresponding values of r_1 and r_2 relating to copolymerisation of the same monomers in bulk form, which was known to occur by a radical mechanism.[170] It was concluded from this that radiation graft polymerisation from the gas phase occurs by a radical mechanism. Most authors accepted this mechanism without further question for all cases of radiation grafting with the exception of grafting in swollen polymer systems at low temperatures.[171–173]

In a series of studies carried out mainly in the 1970s it was shown that radiation graft polymerisation could occur at room temperature even for those monomers which polymerise by an ionic mechanism.[155–169]

The development of these studies resulted from the known fact that certain carefully dried monomers which did not polymerise by a radical mechanism could undergo radiation polymerisation at room temperature by an ionic mechanism.[174,175] These monomers (α-methylstyrene, vinyl n-butyl ether, isobutylene, propylene oxide, acrolein) were also used in the first studies on radiation ionic grafting on to PE, PTFE, and polyvinyl chloride.[155,160,162,165] These monomers, which were dried by the usual methods, including drying over calcium hydride, underwent virtually no grafting on to the above-mentioned polymers during direct liquid-phase grafting at room temperature, whereas after special drying graft polymerisation occurred effectively, the yield of homopolymer at the initial stages of the process being extremely low for radiation liquid-phase graft polymerisation ($\leqslant 1\%$).

In view of its particular importance, the question of the method of drying deserves special consideration. On the basis of a calculation using the value of the radiochemical yields and kinetic polymerisation constants, the upper limit of the water content at which grafting usually occurred was determined. This constituted $\sim 10^{-6}\%$ ($\sim 10^{-8}$ mol litre^{-1}).[158,169] Such a high degree of drying a monomer is a complex technical problem, the more so that such concentrations of traces of moisture in organic liquids cannot even be measured experimentally.[169] It is recommended that all drying operations in grafting from the start to sealing the tubes with modified polymer should be carried out in a completely sealed vacuum system, excluding completely contact with air.[169] The prime importance of careful heating of the glass apparatus at a temperature close to the softening temperature of the glass has been demonstrated.[169] In the choice of suitable drying agents it is necessary to consider not only their ability to absorb water but also the unwanted possibility of initiating on their surface the polymerisation of monomers that are in contact with them. Thus, metallic sodium is a good drying agent, but monomers placed over it

gradually polymerise. Styrene polymerises particularly readily, giving a thin film of polystyrene, which reduces the efficiency of drying, and this occurs not only on the surface of metallic sodium but also on the surface of such efficient drying agents as molecular sieves and barium oxide.[159] For grafting of monomers which only polymerise by an ionic mechanism, drying initially with calcium hydride followed by two or three batches of barium oxide that have been calculated for 6–12 h at 773 K under high vacuum ($\sim 10^{-5}$ mmHg) has proved effective.[155–157, 160] Calcined zeolites of the type CaA and NaA are not very effective. A good drying agent for many monomers, including styrene, is silica gel (KSM-6P grade) with a specific surface area of ~ 500 m^2 g^{-1} and average pore radius of 11.2 Å, which has been activated under vacuum ($\sim 10^{-5}$ mmHg) for 20 h at 773 K.[159,160,162,163,165]

The fact that graft copolymers are obtained at room temperature by radiation graft polymerisation of monomers that do not polymerise by a radical mechanism is evidence for an ionic mechanism.[155–157] In a study of the kinetics of radiation graft polymerisation of vinyl n-butyl ether on to PE, additional evidence for an ionic mechanism was obtained. The initial rate of grafting on a fixed portion proved to be proportional to the dose rate at the first stage and the temperature coefficient of grafting was negative.[157] It was also shown that grafting of vinyl n-butyl ether on to PE by initial irradiation in a "dry", i.e., specially purified, system as opposed to the usual free-radical process on to a "wet" system, i.e., one purified in the normal way, did not occur.[157] It was established using IR spectroscopy in the system PE–acrolein that graft polymerisation in a "dry" system does not occur via a C = C bond as occurs in radical polymerisation but via a C=O bond as in ionic polymerisation.[165]

The nature of the effect of organic solvents on the rate of radiation graft polymerisation in "dry" systems is also confirmation of an ionic mechanism for the process.[162,167] For example, in the system PE–vinyl n-butyl ether grafting is suppressed in electron-donating solvents but is accelerated in electron-withdrawing solvents, which is typical for processes that occur via a cationic mechanism. In this case, for example, in the presence of such a strong electron-withdrawing solvent as 1,2-dichloroethane, grafting of vinyl n-butyl ether, which does not polymerise by a radical mechanism, even takes place in a "wet" system.[162]

The ionic nature of graft polymerisation in "dry" systems has also been confirmed by the direct detection of active sites of an ionic nature in irradiated monomer–polymer systems using low-temperature UV spectroscopy.[164]

Together with monomers that polymerise solely by an ionic mechanism, monomers such as styrene, AN, 4-vinylpyridine, 2-methyl-5-vinylpyridine, phenylacetylene, which can polymerise by both an ionic and a radical mechanism, have also been studied.[159–161,163,166,167,169] When the monomer and the complete system were dried, higher values of the yield of graft polymer were generally obtained compared to "wet" systems. This provided the basis for the proposal of a possible mixed mechanism for grafting, i.e., that it takes place simultaneously by a free-radical and an ionic mechanism.

The fraction of ionic process θ is given by the following equation:[169]

$$\theta = \frac{V_{ion}}{V_{ion} + V_{rad}} = \frac{k_{ig} V_{in}^{ion} k_{rt}^{1/2}}{k_{rg}(V_{in}^{rad})^{1/2}\{(k_{ig}V_{in}^{ion})^{1/2} + k_{ox}[H_2O]\} + k_{rt}^{1/2} k_{it} v_{in}^{ion}}$$

where V_{ion} and V_{rad} are the initial rates for ionic and radical graft polymerisation respectively; k_{rg}, k_{rt}, k_{ig}, k_{it}, and k_{ox} are the growth and termination constants of radical (k_{rg} and k_{rt}) and ionic (k_{ig}, k_{it}, k_{ox}) chains, V_{in}^{rad} and V_{in}^{ion} are the rates of initiation of radical initiation of radical and ionic graft polymerisation.

For monomers with known constants (styrene, for example), figures show the dependence of θ on the dose rate I (Fig. 2) and on the water content (Fig. 3) in the case of grafting on to PE without taking into account chain transfer.[169] It is clear from Fig. 2 that the fraction of the ionic process increases with an increase in dose rate. The complete process can be divided into three bands: a purely radical process, a mixed process, and purely ionic grafting. To achieve ionic grafting over a wide range of dose rates, it is necessary that the water content (or other impurities on which an ionic process can be terminated) should not exceed 10^{-8} mol litre^{-1}. When the concentration of water is $\sim 10^{-4}$ mol litre^{-1}, the transition to a purely ionic grafting only occurs at dose rates exceeding 10^4 Gy s^{-1}.

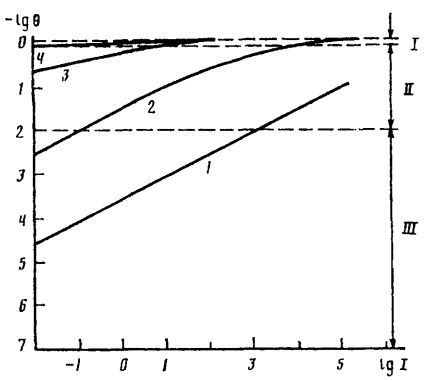


Figure 2. Dependence of the fraction of ionic process on the dose rate (I) with a varying content of water in the system (mol litre^{-1}): *1*, 10^{-2}; *2*, 10^{-4}; *3*, 10^{-6}, *4*, 10^{-8}; $G = 1$; $k_{it} = 10^{11}$; $k_{ig} = 3.5 \times 10^6$; $k_{ox} = 10^{10}$; *I*, purely ionic grafting; *II*, mixed grafting; *III*, radical grafting.[169]

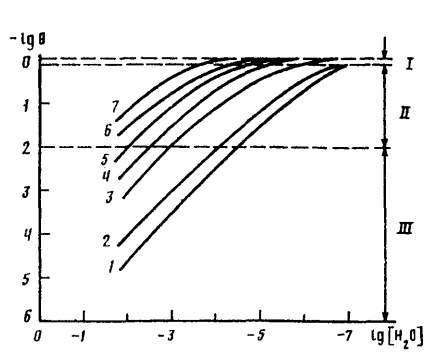


Figure 3. Dependence of the fraction of ionic process on the water content in the system at different dose rates, Gy s^{-1}: *1*, 10^{-2}; *2*, 10^{-1}; *3*, 10; *4*, 10^2; *5*, 10^3; *6*, 10^4; *7*, 10^5; $G = 1$; $k_{it} = 10^{11}$; $k_{ig} = 3.5 \times 10^6$; $k_{ox} = 10^{10}$ (concentration of water, mol litre^{-1}); *I*, purely ionic grafting; *II*, mixed grafting; *III*, radical grafting.[169]

The theoretical dependence of θ on the water content at different dose rates (see Fig. 3) indicates that in order to achieve purely ionic grafting at dose rates of $10^{-2}-10^{0}$ Gy s^{-1}, the water content in the system must be lowered to $10^{-8}-10^{-9}$ mol $litre^{-1}$. With the normal content of water in styrene ($10^{-3}-10^{-1}$ mol $litre^{-1}$) grafting by an ionic mechanism occurs at dose rates of $10-10^{3}$ Gy s^{-1}.

Not only water molecules but also other molecules which accept a positive charge (amines, etc.) act as impurities on which termination of the ionic chains can occur. However, the content of these impurities in the monomers used is negligible.

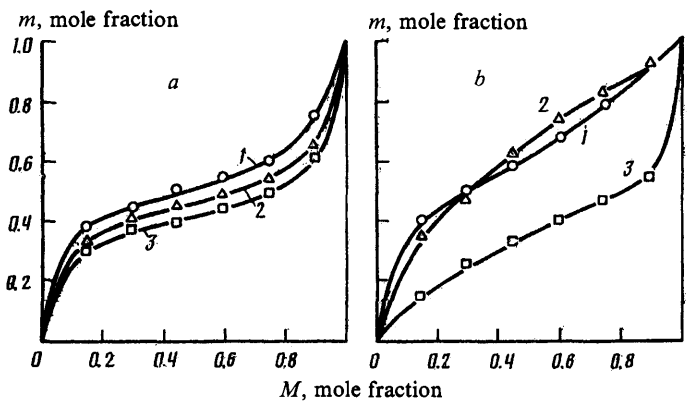


Figure 4. Dependence of the composition of graft copolymer of styrene and acrylonitrile (m) on the composition of the initial mixture of monomers (M); dose rates were 8×10^{-2} Gy s^{-1} (*a*), $(1 \pm 0.2) \times 10^{3}$ Gy s^{-1} (*b*); *1*, without using a solvent; *2*, in methylene dichloride; *3*, in HMPT.[168,169]

Table 1. Constants for graft copolymerisation of styrene and acrylonitrile.[168,169]

Solvent	Dose rate, Gy s^{-1}	Copolymerisation constant	
		r_1	r_2
No solvent	$8 \cdot 10^{-2}$	0.18±0.03	0.16±0.03
CH_2Cl_2	$8 \cdot 10^{-2}$	0.07±0.02	0.22±0.04
HMPT	$8 \cdot 10^{-2}$	0.06±0.02	0.55±0.06
No solvent	$(1 \pm 0.2) \cdot 10^{3}$	0.94±0.08	0.20±0.04
CH_2Cl_2	$(1 \pm 0.2) \cdot 10^{3}$	1.55±0.13	0.26±0.04
HMPT	$(1 \pm 0.2) \cdot 10^{3}$	0.04±0.01	0.83±0.07

In order to confirm the conclusion that the contribution of the ionic process increases with an increase in dose rate, the radiation graft copolymerisation of styrene with AN on to PE was studied under the same conditions at dose rates of 8×10^{-2} and $(1 \pm 0.2) \times 10^{3}$ Gy s^{-1}. The results of determining the composition of the copolymer (Fig. 4) and the copolymerisation constants r_1 and r_2 (Table 1) show that the effect of the solvents differs considerably at low and high dose rates. When a dose rate of $(1 \pm 0.2) \times 10^{3}$ Gy s^{-1} is used, the copolymer is enriched with the styrene component when grafting is carried out in bulk or in the electron-withdrawing methylene dichloride but is enriched with the nitrile component from grafting in the electron-donating hexamethylphosphorotriamide (HMPT). The copolymerisation constants also differ considerably. These results indicate that the radiation graft copolymerisation of styrene with AN on PE takes place at high dose rates with a significant contribution from the ionic mechanism.

The mechanism of initiation or radiation ionic graft polymerisation (cationic and anionic) has been studied insufficiently. It has been suggested[169] that the active sites of cationic graft polymerisation may be radical cations or carbocations that are formed both directly by radiolysis of PE and by the reaction of a monomer radical ion with a radical of the polymer matrix:

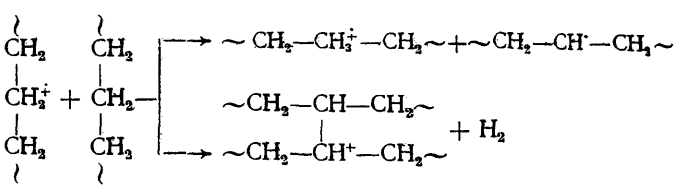
$$R^{\cdot} + M^{\dot{+}} \rightarrow RM^{+}.$$

The first stage in the radiolysis of PE is formation of a radical cation:[169]

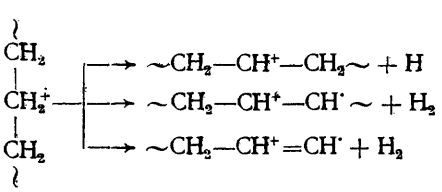
$$\sim CH_2-CH_2-CH_2 \sim \xrightarrow{\gamma} \sim CH_2-\dot{C}H_2-CH_2 \sim + e^{-}.$$

The electron undergoes partial thermolysis and can be captured by structural traps in PE. In adding on the monomer, the radical cation forms an active site for cationic graft polymerisation.

The radical cation of PE can react with a neighbouring polymer molecule to form a cross-link or a carbocation:



Moreover, the radical cation can be converted by elimination of an H atom or H_2 molecule



The elimination of an H atom or H_2 molecule depends on the site of formation of the radical cation. The resulting CH^{+} and $=CH^{+}$ carbocations can also act as initiators of cationic graft polymerisation.

Active sites of an anionic nature are mainly formed by capture of an electron by radicals from the matrix

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

The second route for formation of active anionic sites is reaction of matrix radicals with monomer radical anions:

$$R^{\cdot} + M^{\dot{-}} \rightarrow RM^{-}.$$

All of the schemes shown above for the formation of active sites of ionic graft polymerisation are hypothetical in nature rather than based on experimental confirmation.

There is definite interest in the comparison of the physicochemical properties of radiation grafted copolymers of the same composition which are obtained by different mechanisms, namely free-radical and ionic. Studies of this nature have been carried out in the systems PE–4-vinylpyridine, PE–AN, and PE–styrene.[163] On the thermomechanical curves of PE with 4-vinylpyridine and AN grafted on by a radical mechanism, the flow temperature of the copolymer occurred 17–20 K below that in samples grafted on by an ionic mechanism. Kabanov et al.[163] relate this difference to the higher molecular weight of chains grafted by an ionic mechanism and hence to a stronger interaction between the graft chains. The differential thermal analysis curves of graft copolymers of PE–polystyrene and PE–polyacrylonitrile obtained by different mechanisms do not reveal any significant differences.

In recent years there has been an increase in studies relating a determination of the characteristic of the fundamental stages of radiation polymerisation of monomers adsorbed on the surface of solids, their relationship to the nature of the adsorption of the reactants, and also with the structural features of polymer chains that are formed on the surface of a solid.[71,176–188] A detailed survey of studies on this topic published up to 1984 is given in a review.[71] A considerable number of the studies were conducted on systems with a "weak bond", for which the heat of absorption values were 30–90 kJ mol^{-1}. The adsorption itself is non-localised and reversible in nature and is characterised by a high monomer mobility. Silica (different samples of Aerosil) was used most frequently as the solid matrix and vinyl acetate or MMA were used as monomers. The experiments were carried out at a low concentration of adsorbed monomer, corresponding to one or two monolayers. The initiation rates, the lifetimes of the kinetic curves, and other kinetic parameters of the radical polymerisation of monomers on the surface of silica during radiation initiation were successfully determined in a series of studies.[176–182] The main difficulty was to make a reliable measurement of the initiation rate values and the lifetimes of the kinetic polymerisation chains. Three different methods were used to determine the initiation rates; the results of these are in quite good agreement with each other: 1) determination of the duration of the induction period of polymerisation when an effective non-adsorbing inhibitor such as gaseous oxygen is used: 2) a kinetic method based on the use of expressions from the theory of radical polymerisation which relate the average degree of polymerisation to the kinetic parameters of the process; 3) a method based on the determination of the number of resulting polymer molecules in systems with a low efficiency constant for non-degenerate chain transfer. The lifetimes of the kinetic polymerisation chains were determined from measurements of the length of the initial non-stationary temperature gradient, with the adiabatic temperature gradient method, which essentially involves measurement of the degree of heating of a sample from the heat evolved during polymerisation, being used most frequently.[177–180] Comparison of the kinetic parameters of the radiation polymerisation of vinyl acetate and MMA on the surface of Aerosil and methylated Aerosil containing no hydroxyl groups with the kinetic parameters of radiation liquid-phase polymerisation as reported by Bruk[71] showed that the rate constant for growth decreases approximately by a factor or ten on going from liquid-phase polymerisation to polymerisation on the surface, whereas the rate constant for quadratic termination decreases by a factor of more than 10^3. This results from the diffusion nature of the termination constant and the sharply reduced translational mobility of macroradicals on a surface compared with the gas phase.

On going to systems with a "strong bond", for which localised activated adsorption that is irreversible at room temperature is typical (for example, the adsorption of AA on aminated Aerosil, 4-vinylpyridine on carboxyethylated Aerosil and on Aerosil in the presence of water), as are values of the heat of adsorption of 100–200 kJ mol^{-1} and a low surface mobility of the monomers, a decrease in the rate of growth of chains was recorded because of the strengthening of the adsorptive bond between monomer molecules and the surface of the solid.[183]

A study of the principal mechanisms of radiation adsorptive polymerisation with an increase in thickness of the adsorption layer[184,185] revealed an extremal dependence of the rate of polymerisation on the thickness with a maximum at about four monolayers. It was shown that the rate of initiation decreased with an increase in filling while the rate constant of growth increased rapidly, reaching values typical for mass polymerisation in the region of five to seven monolayers. In a layer of thickness 10–15 monolayers, the rate constant of linear termination was similar to the constant typical for a monolayer, while the rate constant for quadratic termination was approximately 500 times less than that for mass polymerisation.

The conformational features of macromolecules formed by radiation adsorptive polymerisation have been studied.[186–188] It was shown that in systems with a "weak bond" graft macromolecules are formed in conformations that are considerably extended along the surface and can be represented by a model of two-dimensional bundles on the surface. The proportion of units of chains directly synthesised on the surface that are bound to the surface is usually 10–20% higher than in macromolecules adsorbed from solution.

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In the summary of this review it may be concluded that definite progress has been achieved during recent years in the development of methods of radiation graft polymerisation, in studying the mechanism of the processes that occur, and also in the practical application of radiation grafting as a method for modifying polymer materials. At the same time the theoretical principles of improved properties of polymer graft materials have not been sufficiently developed. This mainly relates to the question of the dependence of the physicochemical properties of radiation grafted polymer materials on their structure, the most important component of which is the nature of the structural units formed by macromolecules of the graft polymer and the nature of their localisation in the matrix of the main polymer. In our opinion, in studying this question it is to be expected that fundamentally important new results relating to the solution of problems concerning the preparation of polymer materials with required physicochemical properties will be obtained.

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Inhibitors of the lipoxygenase conversion of polyenoic acids

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ABSTRACT. In this reivew lipoxygenase inhibitors are classified and their inhibitory activity, mode of action, specificity, and chemical synthesis are examined. The future prospects for using them to study enzymatic conversions and the development of antiallergic and antiinflammatory drugs from them are discussed.

The bibliography includes 134 references.

Contents

I. Introduction 482
II. The inhibition of enzymatic oxidative conversion of polyenoic acids 483
III. Different classes of lipoxygenase inhibitors 484
IV. The chemical synthesis of lipoxygenase inhibitors 493
V. Conclusion 498

I. Introduction

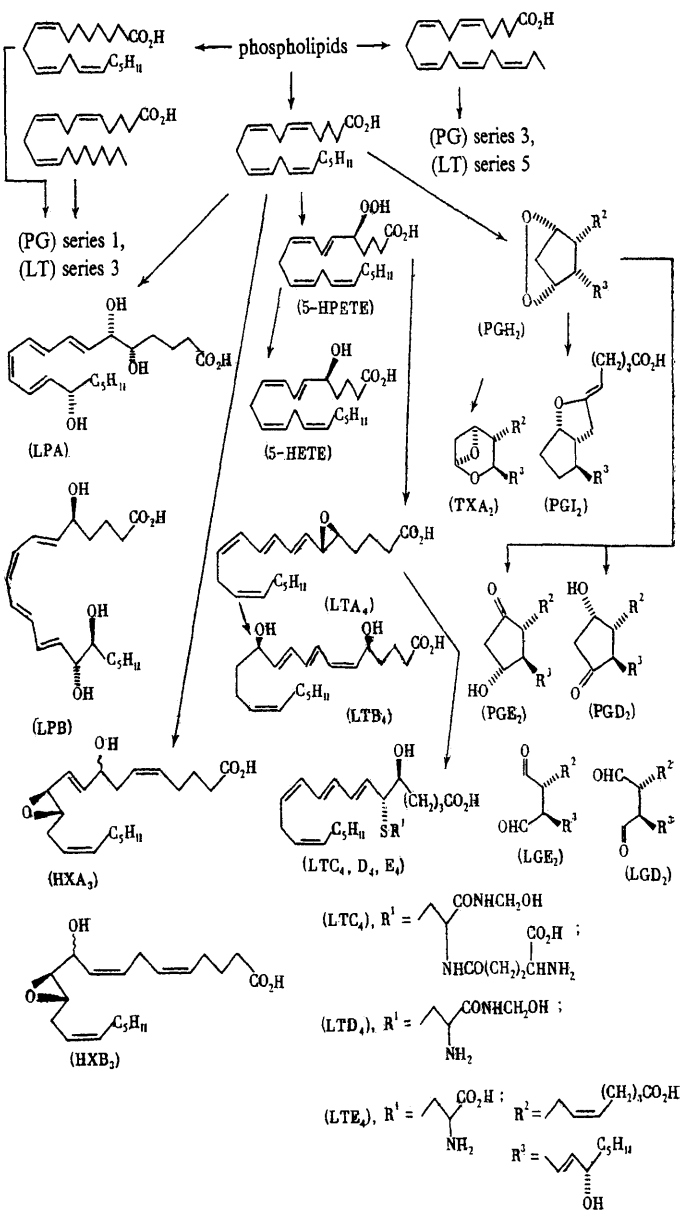
Enzymatic oxidation of eicosapolyenoic acids—arachidonic (5*Z*,8*Z*,11*Z*,14*Z*-eicosatetraenoic), dihomo-γ-linolenic (8*Z*,11*Z*,14*Z*-eicosatrienoic), and timnodonic (5*Z*,8*Z*,11*Z*,14*Z*,17*Z*-eicosapentaenoic) acids—is of considerable interest for a number of reasons.

It forms the basis for the biosynthesis of a whole series of biologically active metabolites, such as prostaglandins (PG), thromboxanes (TX), leukotrienes (LT), lipoxins (LP), hepoxylins (HX), various hydroxy acids (HETE), etc. Moreover, this key reaction of lipid metabolism is interesting from the point of view of its mechanism, which appears to be unique and having no known analogues.

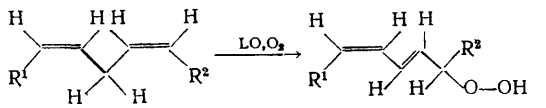
At the present time there are two enzymatic conversion routes of polyunsaturated acids that have been studied to a considerable extent. These are the cyclooxygenase route, in which the biosynthesis of prostaglandins, thromboxanes, prostacyclin (PGI_2), and also levuglandins (LG) takes place through the action of polyenzymatic complexes, and the lipoxygenase route, which results in the formation of acyclic metabolites such as leukotrienes and a number of hydroxy acids, including lipoxins, etc. (Scheme 1).

The mechanism of cyclooxygenase oxidation and cyclooxygenase metabolites have been studied and described in detail in the literature.[1–4] At the same time an active research programme continues on the lipoxygenase metabolism of polyenoic acids, in which the inhibitors of this process play a key role. In the present review the main consideration is given to inhibitors of the biosynthesis of lipoxygenase metabolites and their antagonists in relation to their biological activity and chemical synthesis.

Scheme 1



Lipoxygenases (LO) constitute a group of enzymes containing non-haeme iron that are widely distributed in animals and plants and which catalyse the oxidation of the 1*Z*,4*Z*-pentadiene structure in polyunsaturated fatty acids to a 1-hydroperoxy-2*E*,4*Z*-pentadiene structure:



Lipoxygenase oxidation of polyenoic acids can in principle occur at $2n-2$ carbon positions, where n is the number of *Z*-methylene-separated double bonds. The lipoxygenases known at the present time include 5-LO, which takes part in the biosynthesis of leukotrienes (leucocytes, potato), 8-LO (corals, soybeans), 12-LO (platelets, RBL, PMNL)† and 15-LO (reticulocytes, endothelial cells, soya beans).[5,6]

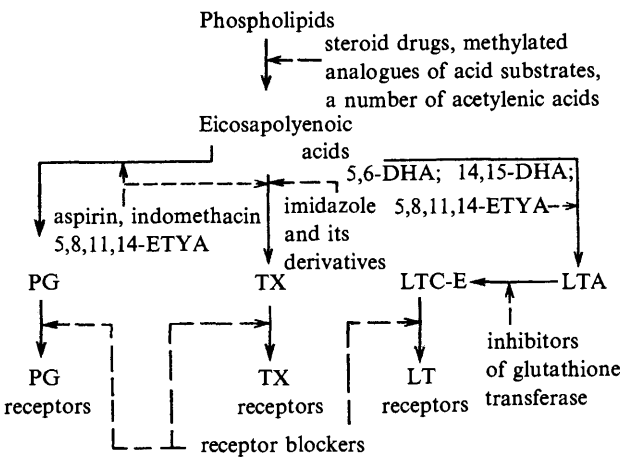
The interest in lipoxygenase metabolites arises because they play a key role in allergic and inflammatory processes. Thus, peptidoleukotrienes (LTC_4, LTD_4, LTE_4) are powerful stimulators of the contraction of smooth muscle, being 10^2-10^3 times more active than histamine.[7] Leukotriene B_4 is an active chemically toxic agent for polymorphonuclear leucocytes, which also causes an increase in vascular permeability and assists the migration of cells and plasma into extravascular space.[7] An important physiological role is apparently played by lipoxins, which stimulate the elimination of the superoxide anion and regulate the immune activity of lymphocytes[8,9] and by hepoxylins, which are potential natural regulators of insulin release.[10]

Research into lipoxygenase oxidation of polyenoic acids will contribute to a better understanding of the physiological role of acyclic eicosanoids and the pathogenesis of the disorders caused by them. A promising approach to the resolution of this problem is the use of inhibitors of the enzymatic conversion of acid substrates in order to study its mechanism. The search for new inhibitors of enzymes in the arichidonic acid cascade is also related to the development of antiallergic and antiinflammatory drugs from them and is therefore of direct practical interest.

II. Inhibition of enzymatic oxidative conversion of polyenoic acids

The release and enzymatic conversion of the precursor acids to their metabolites and the occurrence of biological activity of the latter constitute a complex, interrelated multistage process, which can be controlled at different points (Scheme 2).

Scheme 2



DHA = dehydroarachidonic acid;
ETYA = eicosatetraynoic acid.

Thus, steroid drugs block the release of eicosapolyenoic acids by inhibiting phospholipase A_2, hence preventing any further stage of their enzymatic conversions.[11,12] Well-known inhibitors of the biosynthesis of cyclic eicosanoids are aspirin and indomethacin.[13,14] Disruption of the balance of acid substrates by these compounds results in an increase in the synthesis of leukotrienes.[15] Imidazole and its derivatives have the ability to suppress selectively the synthesis of TXA_2.[16-18] Inhibitors of the enzymatic conversion of polyunsaturated acids that are of considerable interest are compounds which are close to them in structure, including their acetylene analogues[19-31] and acids modified in various ways on the methylene groups[32-34] and carbon skeleton.[35-39]

The regulation of the biological effects caused by eicosanoids can also be achieved through the use of receptor blocking agents such as analogues of PG, TX, LT, and other metabolites,[40-43] which act as their antagonists.

However, Scheme 2 is far from complete in its representation of the problem of pharmacological regulation of the pathway of arachidonic and other eicosapolyenoic acids. Thus, we have a series of enzymatic reactions in which the analogue of a substrate of one enzyme is at the same time the analogue of the product of another enzyme. Therefore, the same compound can act as an inhibitor of different enzymes in the pathway, exhibiting a variable specificity and activity.

As the enzymatic conversion of acid substrates and their metabolites is, in effect, oxidation with oxygen, many antioxidants that act as its inhibitors have been reported.[44-46]

Compounds which are capable of forming chelate complexes with the iron that forms part of the active site of lipoxygenases constitute an important group.[47-49]

Many nitrogen-containing compounds, such as benzene derivatives with nitrogen-containing substituents, nitrogen monocyclic and condensed heterocycles are also known to be inhibitors of enzymes of the arachidonic acid pathway.[50-52]

Thus, at the present time many inhibitors of the oxidation of eicosapolyunsaturated acids have been obtained with different structures and acting at different points of the enzyme pathway,

† RBL = rat basophile leukaemia cells; PMNL = polymorphonuclear leucocytes.

from the release of acid precursors to metabolic reactions of the eicosanoids themselves.

Lipoxygenase inhibitors are valuable agents used to study the functioning of these enzymes, to establish their substrate specificity, the structure of the active site, the nature of the catalytic act, etc. In turn, an understanding of these processes makes it possible to design effectively the structures of compounds which could be used as potential antiallergic and antiinflammatory drugs.

III. Different classes of lipoxygenase inhibitors

1. Analogues of polyenoic acid substrates

An important class of inhibitors of the enzymatic oxidation of natural eicosapolyenoic acids is made up by compounds that are similar to them in structure. These analogues of acid substrates can bind to the active site of the enzyme, but they either cannot be converted to biologically active metabolites (because of particular structural features), resulting in competitive inhibition, or they deactivate the active site of the enzyme, eliminating its capacity to convert natural substrates. At the present time various eicosapolyunsaturated compounds, acids containing triple or cumulated double bonds,[53,54] with methylene groups replaced by heteroatoms (sulphur),[32,33] or modified in a particular way on the carbon skeleton,[35–39] have been synthesised and studied as lipoxygenase inhibitors.

Table 1. Acetylene and allene analogues of acid substrates.

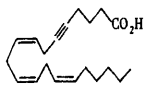
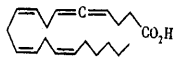
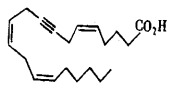
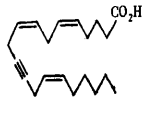
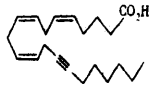
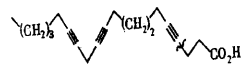
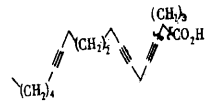
Name	Structural formula	Inhibitory activity	Refs.
5,8,11,14-eicosatetraynoic acid (5,8,11,14-ETYA) (I)		Cyclooxygenase (CO), 5-LO, 12-LO 15-LO	[19—24]
4,7,10,13-eicosatetraynoic acid (4,7,10,13-ETYA) (II)		12-LO	[24, 25]
5,6-dehydroarachidonic acid (5,6-DHA) (III)		5-LO	[53, 54]
4,5-dehydroarachidonic acid (4,5-DHA) (IV)		5-LO	[53, 54]
8,9-dehydroarachidonic acid (8,9-DHA) (V)		weak CO inhibitor (IC_{50} = 50 μM)	[28, 29]
11,12-dehydroarachidonic acid (11,12-DHA) (VI)		CO	[28, 29]
14,15-dehydroarachidonic acid (14,15-DHA) (VII)		15-LO, CO	[28, 29]

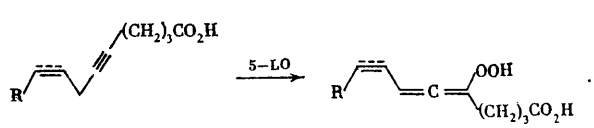
Table 1 (cont'd).

Name	Structural formula	Inhibitory activity	Refs.
5,11,14-eicosatriynoic acid (VIII)		12-LO	[30]
5,8,14-eicosatriynoic acid (IX)		12-LO	[30]
5,8,11,14-heneicosatetraynoic acid ($C_{21:4}$)** (X)		12-LO	[24]
4,7,10,13-heneicosatetraynoic acid ($C_{21:4}$) (XI)		glutathione transferase	[31]
4,7,10,13-nonadecatetraynoic acid ($C_{19:4}$) (XII)		glutathione transferase	[31]
6,9,12,15-docosatetraynoic acid ($C_{22:4}$) (XIII)		12-LO	[25]
7,10,13,16-docosatetraynoic acid ($C_{22:4}$) (XIV)		12-LO	[25]

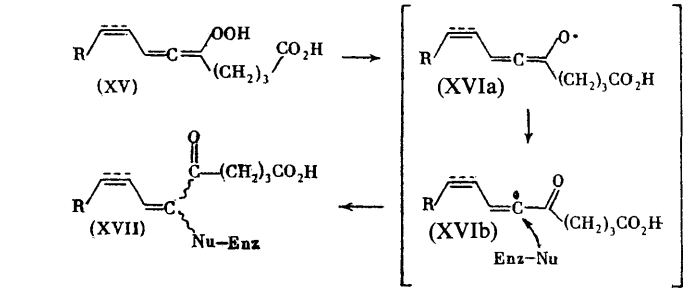
* IC_{50} is concentration of inhibitor producing a 50% loss of enzymatic activity.

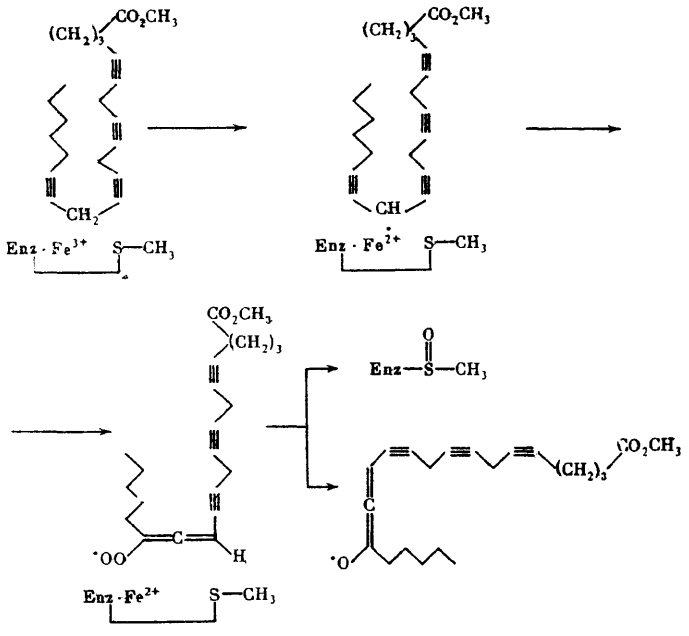
** In $C_{n:m}$ n denotes the number of carbon atoms and m the number of multiple (triple) bonds.

A considerable amount of experimental material on the ability of acetylenic and allenic acids to inhibit enzymes of the arachidonic acid pathway has been collected. The first reports about the inhibitory activity of 5,8,11,14-eicosatetraynoic acid—the acetylene analogue of arachidonic acid—were published in the 1960s.[13] During the following years a considerable amount of work was carried out by different groups of research workers on the synthesis of similar acetylenic fatty acids, some of which as was demonstrated, proved to be selective inhibitors of different lipoxygenases (Table 1).[19–31] Many authors studied the mechanism of inhibition of 5-lipoxygenase by acetylenic acids (5,6-DHA, etc.),[26] which involves the formation of an allenic hydroperoxide as an intermediate:



The unstable allenic hydroperoxide resulting from oxidation of the inhibitor decomposes to form free radicals which irreversibly deactivate the active site of the enzyme. However, different opinions about the exact nature of this step have been advanced. Thus, some authors[7,55,56] maintain that homolysis of the intermediate (XV) results in an active radical product which is attacked by a nucleophile of the active site of 5-lipoxygenase to form a covalent acid–enzyme bond.





Thus, Rapoport et al.[21] regard the deactivation of 15-LO by 5,8,11,14-ETYA as a process that is completely analogous to the deactivation of this enzyme by its reaction product—the hydroperoxy acid—but with the important distinction that deactivation with the acetylenic acid results from each act of substrate conversion.

It should be pointed out that both schemes put forward are based on the formation of the vinyl hydroperoxide (XV), which accords well with the fact that 4,5-dehydroarachidonic acid (4,5-DHA)—the allenic isomer of 5,6-DHA—is a powerful inhibitor of 5-LO.[53,54]

Deactivation of lipoxygenases with acetylenic and allenic acids depends on the time of incubation with the inhibitor and is irreversible, since neither strong dilution of the given system nor subsequent addition of excess substrate (50:1) could regenerate the activity of the enzyme.[21]

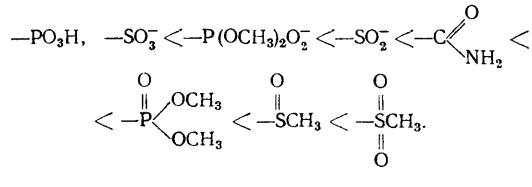
The effect of acetylene analogues of natural fatty acids as inhibitors and their specificity are determined by the number and position of double bonds. In spite of the obvious differences in the steric structure of acid substrates and the polyynoic acids that correspond to them,[50] replacement of particular double bonds leads, as a rule, to inhibition of the enzymatic conversion precisely at those positions. Thus, an obvious disadvantage of 5,8,11,14-ETYA (I) is its lack of specificity since it deactivates both cyclooxygenase and a number of lipoxygenases to approximately the same degree.[30]

At the present time a number of tetraynoic acids have been synthesised with a different configuration of triple bonds to that in natural acids and a different number of carbon atoms, and they exhibit considerable selectivity.[24,25] Thus 4,7,10,13-eicosatetraynoic acid (II) and 5,8,11,14-heneicosatetraynoic acid (X) inhibit the 12-lipoxygenase oxidation of arachidonic acid to 12-HPETE without any significant effect on the cyclooxygenase oxidation to TXB_2 in human platelets.[24] The IC_{50} values relating to 12-lipoxygenase and cycloxygenase were determined experimentally for 4,7,10,13-ETYA, being 7.8 μM and 100 μM respectively.[25] Evidently acids (II) and (X) can serve as selective modulators of 12-lipoxygenase oxidation in platelets and other tissues.

Other polyynoic acids have also been synthesised, in particular 6,9,12,15-docosatetraynoic acid (XIII) and 7,10,13,16-docosatetraynoic acid (XIV), which fairly selectively inhibit 12-LO (IC_{50} CO/IC_{50} LO is 336.8 for (XIII) and 333.3 for (XIV).[25] It is not excluded, however, that the mechanism of the action of acetylenic acids (II), (X), (XIII), and (XIV) is different to that for 5,8,11,14-ETYA. Thus, according to the results of Corey,[31] 4,7,10,13-heneicosatetraynoic acid (XI) and 4,7,10,13-nonadecatetraynoic acid (XII) block the formation of SRS (slow reacting substance) by inhibiting glutathione transferase, namely, at a later stage of biosynthesis.

Thus, these acetylenic and allenic inhibitors act as irreversible inhibitors of the enzymatic conversion of natural polyenoic acids to their metabolites, since they act as suicide substrates, the oxygenation of which is related to an irreversible loss of enzymatic activity.

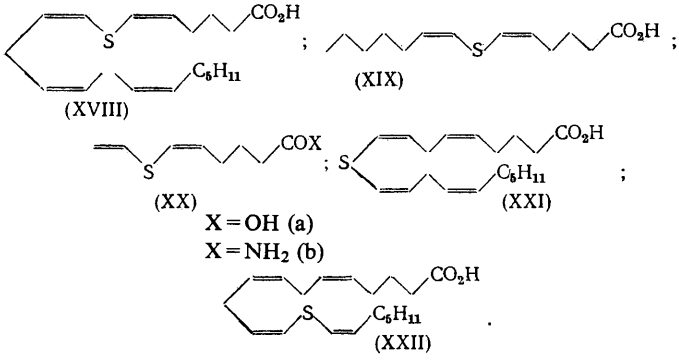
Polyunsaturated acids can be incorporated into the phospholipids of cell membranes, which considerably reduces their activity as inhibitors of lipoxygenase oxidation *in vivo* since phospholipids are not lipoxygenase substrates. A number of analogues of 5,6-DHA (III) containing functional groups other than a carboxyl group have been obtained. The rate of deactivation of 5-LO during aerobic incubation increased in this case according to the following series:



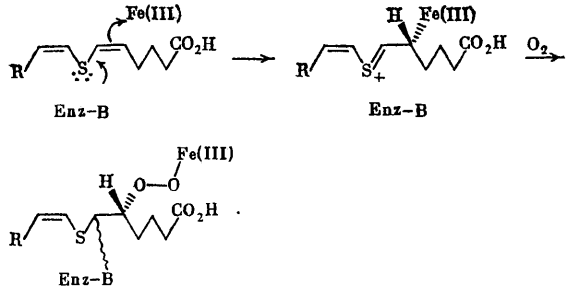
In the opinion of Corey et al.,[26] the inhibition of 5-LO by these 5,6-DHA derivatives indicates that the presence of an anionic group such as carboxyl is not absolutely essential for the binding of acid with enzyme.

Since the mechanism of the catalytic action of lipoxygenases involves the elimination of a hydrogen atom from a bis-allyl methylene group [C(7), C(10), C(13) for arachidonic acid] as the first stage, modification of these positions, making this stage of enzymatic catalysis impossible, opens up extensive possibilities for the development of competitive and non-competitive inhibitors that have the structure of acid substrates with modified methylene groups. This type of modification can be achieved either through the introduction of heteroatoms (sulphur)[32,33] at this position or by replacement of the hydrogen atoms that are prone to elimination with different substituents,[21] and also by converting them into part of ring systems.[38,39,57,58]

In 1985 a series of polyenoic acids containing sulphur atoms at the positions of primary attack by an enzyme of physiological substrates was synthesised by Corey et al.[31–33] and studied as potential inhibitors. It was shown that incubation of 5-LO from RBL-1 with compounds (XVIII)–(XX) leads to the irreversible deactivation of the enzyme, with deactivation showing a dependence on time.



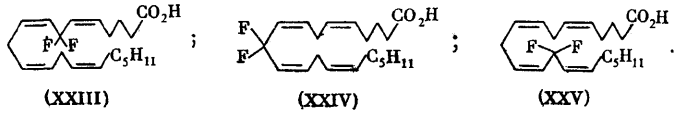
A mechanism for the inhibition of 5-LO by acids (XVIII)–(XX) has been put forward.[32] These compounds do not contain a proton that can be eliminated at the 7-position, but the electron-donating capacity of the thiadivinyl residue, according to Corey et al.,[32] is sufficiently high for direct electron transfer to Fe(III) on the active site of the enzyme to be able to occur, and oxidation can subsequently take place:



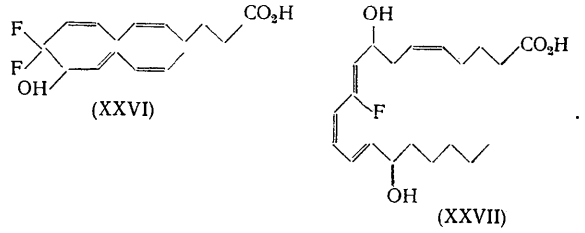
The intermediate formed by oxidation is attacked by the proton-acceptor B^- in the active site, resulting in covalent bonding of the inhibitor[32,33] and is the cause of the irreversible deactivation of the enzyme. The effect of thia-acids (XVIII)–(XX) on cyclooxygenase (isolated from rat testes) was also studied, from which acids (XVIII)–(XX) exhibited properties of competitive inhibitors.[32]

Corey et al.[33] also described the syntheses by 10-thiaarachidonic acid (XXI) and 13-thiaarachidonic acid (XXII). In accordance with the proposed mechanism, it would be reasonable to expect that 13-thia-acid (XXII) would be an irreversible inhibitor of 15-LO. This assumption was confirmed experimentally for 15-LO,[31] which is also fully consistent with the mechanism and substrate specificity of the enzyme.

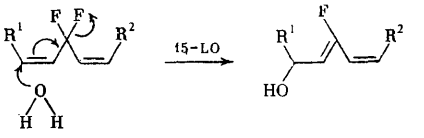
The difluoro analogues of arachidonic acid (XXIII)–(XXV) were also studied as inhibitors that are modified on the bis-allyl methylene group:[34,59]



It would be logical to expect from the similarity of the van der Waals radii of hydrogen and fluorine that compounds (XXIII)–(XXV) would be either substrates or (because of the inability of the enzyme to cause homolytic cleavage of the C–F bond) specific competitive inhibitors of different LOs. 10,10-Difluoroarachidonic acid (XXIV) was studied as a substrate of cyclooxygenase and 15-lipoxygenase of soybeans.[59] In the first case acid (XXIV) was converted to 10,10-difluoro-11-HETE (XXVI) and 10-fluoro-8*S*,15*S*-di-HETE (XXVII). Cyclisation to a PG did not occur. Incubation of the same acid with soybean 15-LO resulted in the formation of 10-fluoro-8*S*,15*S*-di-HETE (XXVII):



A mechanism of general base-catalysed substitution for the formation of HETE (XXVI) and (XXVII) has been proposed, the driving force of which is formation of a stable fluorodiene system:[59]

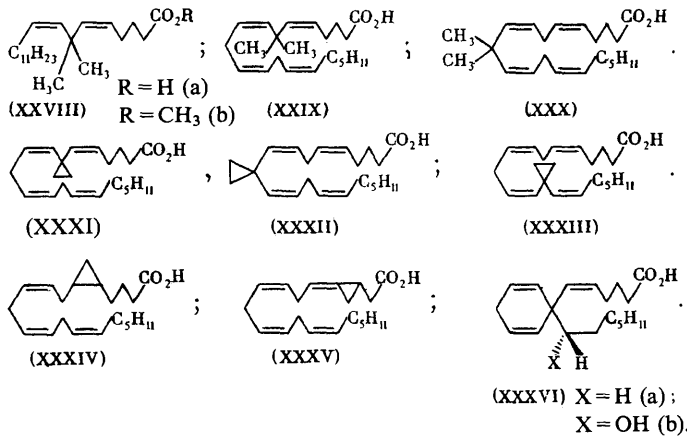


No studies on acids (XXIII) and (XXV) as inhibitors of 5-LO and 15-LO were carried out.[59]

This approach to the development of inhibitors also involves the modification of the carbon skeleton of acid substrates, for which a clear dividing line cannot always be drawn between modification of just methylene groups and more general structural changes.

Many analogues of arachidonic acid have been synthesised, in which the methylene positions, which are subject to attack in the natural acids, are either blocked with alkyl substituents or form part

of cyclic cyclopropane structures, and prove to be competitive lipoxygenase inhibitors [compounds (XXVIII)–(XXXIII)].



Acid (XXVIIIa) at a concentration of 50 μM inhibited 5-LO of human RBL-1 and PMNL cells by 43% and 26% respectively. Its methyl ester was somewhat more active, inhibiting the same enzyme by 74% and 50% respectively.[36] The action of this inhibitor was selective, since at this concentration there was no inhibition of either 12-LO or cyclooxygenase.[36]

gem-Dimethyl derivatives of arachidonic acid (XXIX) and (XXX) also proved to be fairly weak inhibitors of 5-LO (Table 2). However, all of the acids (XXVIIIa)–(XXX) were powerful inhibitors of LT biosynthesis.[23]

Table 2. Inhibitory activity of *gem*-dimethyl analogues of arachidonic acid.[37]

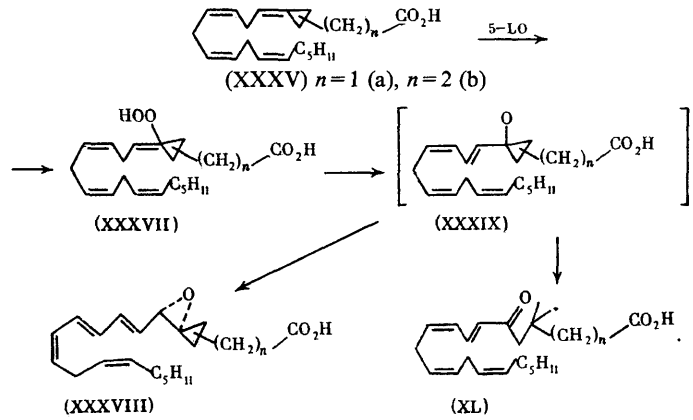
Compound	Inhibition of biosynthesis, % at 10 μM	5-LO inhibition, % at 100 μM	Cyclooxygenase IC_{50}, μM	Phospholipase A_2, %
(XXVIIIa)	100	56	1000	100 (14)
(XXIX)	100 (1–3)	66 (68)	225	100 (14)
(XXX)	98	42	13	100 (14)

Note. IC_{50} values given in brackets.

Thus, it is thought that compounds (XXVIII)–(XXX) block the formation of LT mainly by inhibition of phospholipase A_2 rather than inhibition of 5-LO.[37]

In the opinion of Nicolaou et al.[38,39] by blocking the bis-allyl positions of eicosapolyenoic acids through the introduction of an ethano group in the form of a cyclopropane ring, it is possible not only to achieve the purpose in hand but also to increase the rigidity and stability of the carbon skeleton of arachidonic acid and hence provide a higher biological activity.[38] Studies on the inhibitory activity of ethanoarachidonic acid have been carried out.[39] It was shown that 7-ethanoarachidonic acid (XXXI) is a weak inhibitor of 5-LO (34% inhibition at 100 μM).[60]

A number of methylenecyclopropane analogues of arachidonic acid (XXIV) and (XXXVa) have been synthesised.[57,60] It is assumed that acids (XXXVa) and (XXXVb) can be converted by 5-LO to the HPETE-type hydroperoxide (XXXVII), which can deactivate the enzyme in different ways:[57]



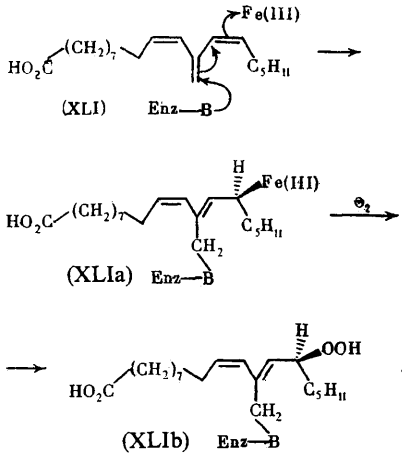
Enzymatic dehydrogenation results in the formation of the reactive oxaspiropentane analogue of LTA_4—(XXXVIII). The additional strain in the carbon skeleton introduced by the cyclopropane ring and the additional cyclopropylcarbinyl stabilisation of the carbonium ion formed by scission of epoxide (XXXVIII) result in the formation of an intermediate at the active site of the enzyme which can bind to nucleophiles contained in it. The alternative conversion of hydroperoxide (XXXVII) to the intermediate (XXXIX) by a homolytic mechanism gives enol (XL) by fragmentation of the cyclopropane ring. Enol (XL) can also irreversibly deactivate the enzyme by binding to a nucleophile.[57] By comparing the ability of compounds (XXXVa) and (XXXVb) to inhibit the synthesis of leukotrienes it would also be possible to determine the preferred conformation of the acid substrate for binding to the enzyme, since these compounds may be regarded as conformers of the C(1)–C(4) carboxyl chain of arachidonic acid that are fixed in a given orientation relative to the 5,6-double bond.[29] Acid (XXXIV) was shown to be inactive as an inhibitor of 5-LO.

By analogy with the *gem*-dimethyl[35,36] and cyclopropane[38,39,57,60] analogues of eicosapolyenoic acids, the 1,1-disubstituted 2,5-cyclohexadienes (XXXVIa) and (XXXVIb) have also been proposed.[58]

Compound (XXXVIa) inhibited 5-LO from RBL-1 (IC_{50} = 120 μM) and inhibited cyclooxygenase to a lesser degree (IC_{50} = 150 μM). By introducing a hydroxyl group on to C(15) it was possible to increase significantly the activity of this structure as an inhibitor of 5-LO (IC_{50} = 6 μM) while its activity towards cyclooxygenase remained unchanged.

In 1986, 12-methylidene-10*Z*,13*Z*-nonadecadienoic acid (XLI), an irreversible inhibitor of soybean 15-lipoxygenase, was synthesised.[31,61] Incubation of acid (XLI) with the enzyme resulted in a time-dependent deactivation. The kinetic characteristics were similar to those in the incubation of 13-thiaarachidonic acid (XXII) and soya bean 15-LO.[61]

The following mechanism of deactivation has been proposed:



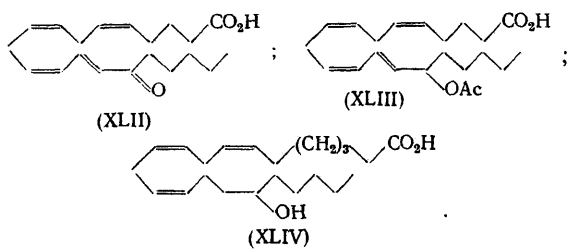
In Corey's opinion[31,61] the activity of this inhibitor is also due to the absence of oxygen that can be eliminated while at the same time there is the ability to be activated on the active site to form intermediates that attack and form covalent bonds with certain functional groups of the active site.

2. Analogues of lipoxygenase metabolites

In addition to the development of various modified acid substrates, a rational approach to the question of obtaining lipoxygenase inhibitors is the use of analogues of lipoxygenase metabolites (leukotrienes, hydroxy acids, etc.).

Thus, in 1980 Vanderhoek et al.[63] reported that 15-hydroxyeicosatetraenoic acid (15-HETE) acts as an inhibitor of 5-LO [62] and 12-LO.[63] These findings served as a basis for the development of a whole class of lipoxygenase inhibitors.

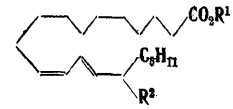
With the aid of three-dimensional computer models, a number of 15-HETE analogues were selected, synthesised, and tested for biological activity:



All modifications directly to the 15-hydroxy group resulted in a reduction of activity. Thus, the 15-keto (XLII) and 15-acetoxy (XLIII) analogues had an IC_{50} (RBL-1, 5-LO) of 26 and 17 μM respectively compared to 7.3 μM for 15-HETE. Extension of the carbon chain by 2 atoms [compound (XLIV)] also reduced the activity.

It was established that 15-HETE analogues that contain a 5*Z*,8*Z*-diene system inhibit 5-LO, by acting as alternative substrates.[64] Research was then initiated on inhibitor compounds that were devoid of this structure. The prototype of this series — 15-hydroxy-11*Z*,13*E*-eicosadienoic acid (15-HEDE) — is a comparatively weak inhibitor (IC_{50} = 26 μM).[64]

Table 3. Inhibitory activity of 15-HEDE derivatives.[64]

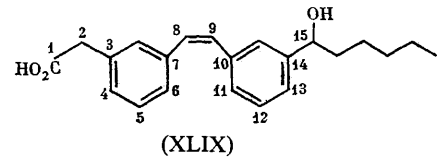


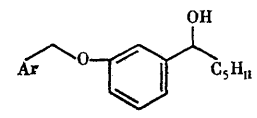
Compound	R^1	R^2	IC_{50}, μM
(XLV)15 *S*	OH	OH	26
(XLVI)15 *S*	OH	OAc	76
(XLVII)	OH	=O	55
(XLVIII)	OH	H	73

The stereochemistry of the 15-hydroxy group does not appear to be important for inhibition since the natural *S*-isomer and racemic 15-HEDE [64] showed no difference in activity (Table 3). Acetylation and oxidation of the hydroxy group reduced the activity by a factor of 2–3.[64]

Thus, research into 15-HEDE analogues did not yield any active inhibitors of 5-LO, but it confirmed the possibility that the inhibitory activity of compounds lacking the 1*Z*,4*Z*-pentadiene structure that is typical for lipoxygenase substrates would be retained.[60] It was shown that although there are certain structural features in the analogues of 15-HETE and 15-HEDE (the presence of a free carboxyl group, the length of the carboxyl- and ω-chains, the absence in the latter of polar groups, etc.), no single part of the molecule plays a decisive role in determining inhibitory activity.[64] These findings indicate, according to Haviv et al.,[64] that there are many sites for binding of these inhibitors to an enzyme.

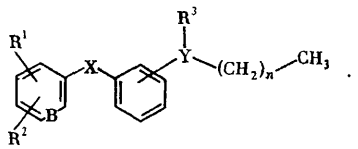
By using three-dimensional computer models of 15-HETE, it was possible to establish the potential application of analogues in which the 11*Z*,13*E*-double bonds were replaced by a benzene ring:[65]





Replacement of the 5- or 8-double bond [compounds (XLIX) and (L) respectively], which involves the formation of a C(3)–C(7) bridge (XLIX) and the introduction of an ether bond at C(8)–C(9) (L) with retention of a good isosteric conformity with 15-HETE is

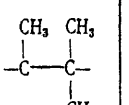
less apparent.[65] On the basis of the stereochemical arguments presented by Musser et al.,[65] 54 compounds with the general structure (LI) were synthesised:



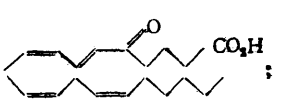
(LI)

All of the compounds with structure (LI) were tested as inhibitors of 5-LO from rat neutrophiles (Table 4). The most active inhibitors were compounds (LIa) and (LIb) (IC_{50} of 0.12 and 0.13 μM respectively).

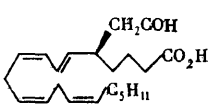
Table 4. Inhibitors (LIa) and (LIb).[65]

Compound	R^1, R^2	B	X	Y	R^3	*h*
(LIa)		N	CH_2O	$-CH_2CH_2-$	OH	3
(LIb)		N	CH_2O		OH	3

The inhibition of 5-LO by the following 5-HETE analogues has been reported:[66]



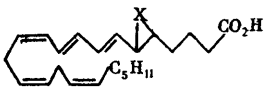
(LII)



(LIII)

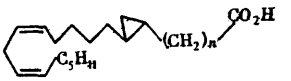
Both compounds are inhibitors of 5-LO from guinea pig PMNL (the second being very weak), with IC_{50} of 20 μM (LII) and 100 μM (LIII).

A number of analogues of LTA_4 which can inhibit 5-LO have been synthesised.[66–69] The carbon analogue of LTA_4—(LIVa)—is an active inhibitor of 5-LO (IC_{50} = 3 μM).[68] Other cyclopropane analogues which differ according to the length of the carbon chain have been reported.[7,66] The position of the cyclopropane ring affects the inhibitory activity of the compounds much less than the presence and position of multiple bonds.[66] The IC_{50} values of compounds (LV) and (LVI) were 20–30 μM, while saturation of the double bonds results in an almost inactive product (LVII) (IC_{50} = 100 μM).



(LIV)
X = CH_2 (a)
X = S (b)
X = NH (c)

;



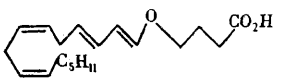
(LV), *n* = 2;
(LVI), *n* = 4.



(LVII)

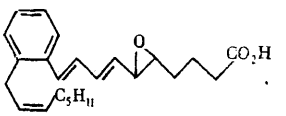
The thio analogue of LTA_4—(LIVb)—is a weak inhibitor of 5-LO (IC_{50} = 65 μM).[66] The synthesis of the aziridine (LIVc) has been reported but its biological activity is not mentioned.[69]

In addition, (LVIII) and (LIX)—two LTA_4 analogues with a modified carbon skeleton—have been synthesised.



(LVIII)

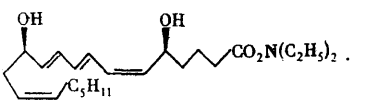
;



(LIX)

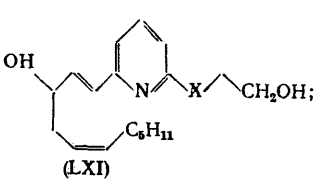
It is thought that their activity is due to the impossibility of opening the epoxide ring because of the modified structure, which excludes their subsequent conversion to LTB_4 and the peptidoleukotrienes LTC_4, LTT_4, and LTE_4.[70]

LTB_4 analogues that act as inhibitors of 5-LO have not been prepared up to the present time. Antagonists of LTB_4 have been reported. The LTB_4 diethylamide (LX) inhibits the degranulation of neutrophiles caused by LTB_4 at concentrations of 10^{-6}–10^{-7} M.[7]

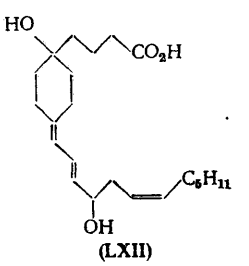


(LX)

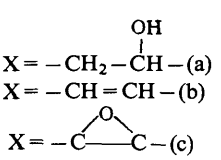
A number of stereoisomers of LTB_4, such as 15*S*,12*S*-di-HETE, proved to be capable of inhibiting 5-LO from PMNL.[71] A number of ring-containing analogues of LTB_4 have been reported; (LXI) [72] and (LXII)[73] act in competition to LTB_4.



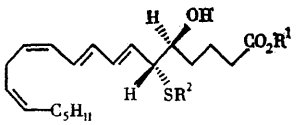
(LXI)



(LXII)



Only a few peptidoleukotriene analogues that inhibit 5-LO are known.[74] However, the absence of a common method for determining the activity of 5-LO led Japanese research workers[74] to the conclusion that the activity of compounds with the general structure (LXIII) may in fact be due to their inhibition of glutathione transferase.



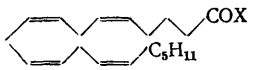
(LXIII) $R^1 = H, CH_3$; $R^2 = CH_2C_6H_5, C_3H_7$, iso-C_4H_9.

3. Compounds which form chelate complexes with Fe(III)

The enzyme mechanism of the lipoxygenase reaction is associated with the presence of iron [Fe(III)] at the active site of the enzyme.[67,75] These findings formed the theoretical basis for the synthesis of different eicosapolyenoic acid derivatives and compounds of a different structure that can form chelate complexes with Fe(III), hence deactivating the enzyme.

An additional argument to support the key role of iron in the act of catalysis is the theory put forward by Corey[76,77] concerning the formation of an organoiron intermediate with the substrate at the active site of the enzyme.

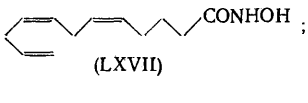
The first compounds to be studied as inhibitors of this type were hydroxamates of arachidonic acid, which are ligands capable of coordinating with Fe(III) ions ($K_{assoc} = 10^{-12}$). The K_m values were consistent with competitive inhibition.[78] However, not one of these compounds (LXIV)–(LXVI) acts as a substrate of 5-LO, although they are some of the most powerful inhibitors of it. Thus, the EC_{50}‡ values for these compounds are 2.2, 0.3 and 0.2 μM respectively:[78]



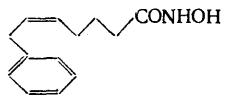
(LXIV), X=NHOH; (LXV), X=N(CH$_3$) OH,
(LXVI), X = N (t-C$_4$H$_9$)OH.

It is the hydroxamate groups which are thought to be responsible for bonding with the ferric ions participating in the catalytic cycle, so that the presence of the complete carbon skeleton of eicosapolyenoic acids is not absolutely essential for inhibitors of this type.[78,79]

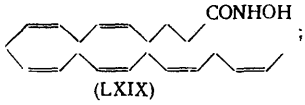
This is supported by the fact that compounds (LXVIII)–(LXX) (obtained by total synthesis) are very powerful inhibitors of 5-LO (EC_{50} = 1.9 μM).[78]



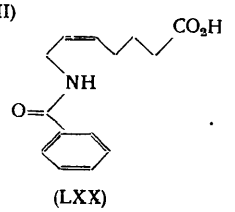
(LXVII)



(LXVIII)



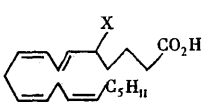
(LXIX)



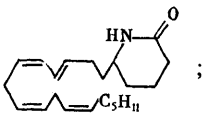
(LXX)

‡ EC_{50} is the effective concentration of inhibitor that produces a 50% loss of enzyme activity.

The 5-hydroxyamates of 6*E*,8*Z*,11*Z*,14*Z*-eicosatetraenoic acid were subsequently synthesised and tested as inhibitors of 5-LO:[80,81]



(LXXI), X = CONHOH;
(LXXII), X = CH_2CONHOH;
(LXXIII), X = NNHCONH$_2$;
(LXXIV), X = NNHCSNH$_2$;
(LXXV), X = SH.

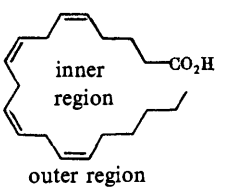


(LXXVI)

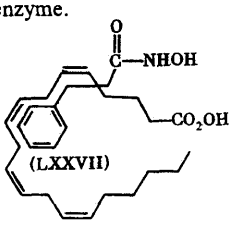
Thus, compounds (LXXI) and (LXXII) proved to be powerful inhibitors of 5-LO in a supernatant of homogenised RBL-1 cells (IC_{50} = 1.4 and 0.19 μM respectively).[80] Hydroxamate (LXXII) is over ten times more active than the arachidonic acid hydroxamate (LXIV) (IC_{50} = 0.19 and 2.2 μM respectively).[80,81] Thus, transfer of the hydroxamate functional group to the C(5) position considerably increases the ability to chelate with ferric ions. The effect of replacing the hydroxamate functional group by others was also studied, taking into account the possibility that they could interact with the active site of the enzyme in addition to chelation with Fe(III).[81] The most active of these proved to be the semicarbazide (LXXIII), thiosemicarbazide (LXXIV), the thiol (LXXV) (IC_{50} = 7.0, 7.9, and 7.6 μM respectively). The cyclic lactam (LXXVI) also proved to be an active inhibitor, being three times more active (IC_{50} = 10.0 μM) than its linear analogue.[81]

However, although the compounds reported by Corey et al.[78,80,81] are extremely active inhibitors of 5-LO, it is unlikely that they could be of therapeutic use.[79] As analogues of arachidonic acid they would tend to undergo chemical oxidation and would be rapidly degraded *in vivo*. Therefore, there is considerable interest in more stable hydroxamates with quite a simple structure,[79] which nevertheless retain the high activity which was demonstrated for the arachidonic acid analogues described above.

The approach of Summers et al.[79] is based on a selection of compounds that can effectively bind to the active site, which may be regarded as consisting of non-haeme Fe(III), a hydrophobic region, and a section for bonding of the carboxyl group of the substrate,[82] because of the correspondence of their structure to the conformation of arachidonic acid bound to the enzyme.

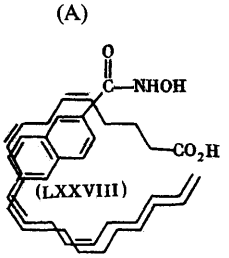


(A)



(LXXVII)

(B)



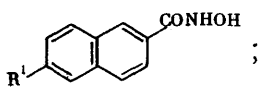
(LXXVIII)

(C)

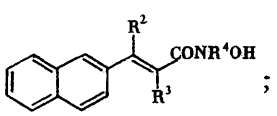
The hypothetic conformation (A) of arachidonic acid at the active site[22,79] is shown above together with the "superposition" of simpler aromatic hydroxamates on it in (B) and (C). It is clear that in case (C) the "superposition" is considerably more precise, which is in agreement with the experimental results.[79] In selecting inhibitors, the authors have attempted, other conditions being equal, to give preference to those compounds and their isomers which occupy the volume in the inner region to a lesser extent.

ω-Phenylalkyl- and ω-naphthylalkyl-hydroxamates were studied as inhibitors of this type (sources of enzyme activity—supernatant RBL-1), and the latter were, as a rule, more active,[79] which is consistent with a greater affinity of the enzyme towards more lipophilic compounds. The introduction of a methylene group between the benzene ring and the carboxyl group increased the activity of the compounds. A study of the effect of substituents in the aromatic systems showed that derivatives with electron-withdrawing groups are more active. Any modification of the hydroxamate function (apart from methylation) reduce the activity of the inhibitors.[79]

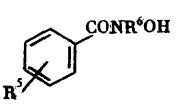
Thus, it was shown that even compounds with a simple structure that contain the hydroxamate group can be powerful inhibitors of 5-LO:



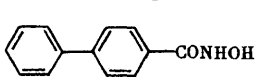
(LXXIX), $R^1 = O(CH_2)_3CH_3$;
(LXXX), $R^1 = O(CH_2)_2CH{=}CH(CH_2)_4CH_3(Z)$;



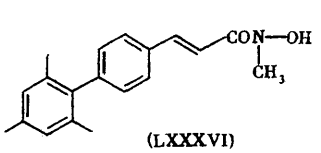
(LXXXI), $R^2 = CH_3$, $R^3 = H$, $R^4 = CH_3$,
(LXXXII), $R^2 = H$, $R^3 = H$, $R^4 = Ph$;



(LXXXIII), $R^5 = p$-(1-naphthyl);
$R^5 = p$-(2,4,6-trimethylphenyl);



(LXXXV)

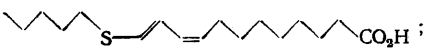


(LXXXVI)

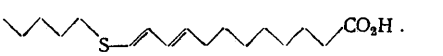
Compound	(LXXIX)	(LXXX)	(LXXXI)	(LXXXII)	(LXXXIII)	(LXXXIV)	(LXXXV)	(LXXXVI)
IC_{50}, μM	6.5	2.9	0.12	0.052	0.18	0.29	0.41	0.022

Compound (LXXXVI) is one of the most active inhibitors of 5-LO to be studied.[78,79]

Sulphur-containing polyunsaturated acids can also be grouped with inhibitors that chelate with iron.[48] In the opinion of Funk et al.,[48] the effect of these compounds is derived from a similarity in their structure to substrates of LO as well as their ability to chelate with Fe(III):



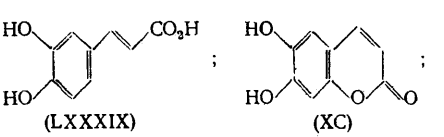
(LXXXVII)



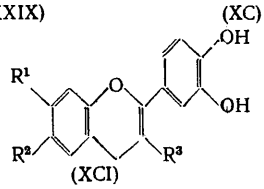
(LXXXVIII)

13-Thia-9*Z*,11*E*-octadecadienoic acid (LXXXVII) and 13-thia-9*E*,11*E*-octadecadienoic acid (LXXXVIII) were tested as inhibitors of soybean 15-LO and they exhibited the properties of competitive inhibitors.[83]

The ability of caffeic acid (LXXXIX) and its derivatives,[84] esculetin (XC),[85] and certain flavonoids (XCI) [86] to form chelate complexes with Fe(III) is known, their activity as inhibitors of 5-LO being related to this:



(LXXXIX) (XC)



(XCI)

cirsilol $R^1 = H$, $R^2 = OCH_3$, $R^3 = OCH_3$ (a);
pedalitin $R^1 = H$, $R^2 = OH$, $R^3 = OCH_3$ (b);
quercetin $R^1 = OH$, $R^2 = H$, $R^3 = OH$ (c).

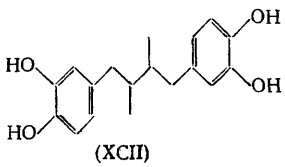
The mechanism of complexation of flavonoids with Fe(III) is unclear, it is also possible that they act through a dual mechanism—as chelating agents of Fe(III) and as antioxidants, which they behave as at the same time (see below).[7,86]

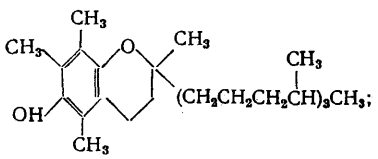
It should be mentioned, however, that 5-LO is definitely not the only iron-containing enzyme of the arachidonic acid pathway (cyclooxygenase, 12-LO, and 15-LO also contain it).[7,31,75,87] Hence there is no reason to expect high specificity from inhibitors of this type.

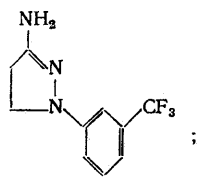
4. Antioxidants

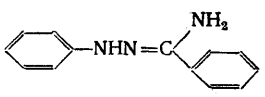
Since the lipoxygenase reaction is, in essence, the oxidation of acid substrates with oxygen, it was natural that many antioxidants should prove to be inhibitors.

Virtually all known antioxidants inhibit 5-LO to a given extent, these include sterically hindered phenols [nordihydroguaiaretic acid (NDGA)] (XCII), α-tocopherol (XCIII), flavonoids (XCI),[88] etc.

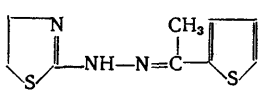

(XCII)

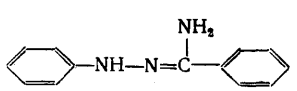

(XCIII)


(XCIV)


(XCV)

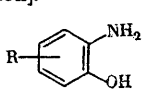
A separate group is made up by the hydrazone antioxidants BW-755C (XCIV) [89] and CBS-1114 (XCV) [90] and hydrazones (XCVII) and (XCVIII):[91]


(XCVI)

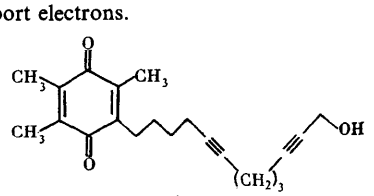

(XCVII)

A characteristic feature of these inhibitors is the absence of selectivity towards LO. Thus, compounds (XCVII) and (XCVIII) inhibit 5-LO, 12-LO, and cyclooxygenase to virtually the same extent.[91]

o-Aminophenols with the general structure (XCVIII) have also been reported[92] as antioxidant inhibitors of 5-LO. However, a dual mechanism, similar to that for flavonoids, cannot be excluded for their mode of action [chelation with Fe(III) and inhibition of oxidation].


(XCVIII)

A special group of antioxidants is made up by the so-called Takeda quinones,[93] which are similar to ubiquinones in structure. There is most interest in quinone AA-861 (XCIX), which has the highest selectivity in this series and inhibits 5-LO (IC_{50} = 1 μM) without having any significant effect on cyclooxygenase and 12-LO at concentrations up to 10 μM (when 5-LO retains only 3% activity). This compound has passed clinical trials as a potential drug for the treatment of bronchial asthma.[7] Its mode of action has not been established, although ubiquinone is known for its ability to transport electrons.


(XCIX)

A correct interpretation of the role of antioxidants as potential pharmacological drugs should evidently be made on the basis of recently published reports concerning the role of the so-called active forms of oxygen—AOS (active oxygen species) (superoxide anions, peroxides, hydroxyl and ferryl radicals, etc.)[94] in diseases such as cancer, cardiovascular disorders, allergic and inflammatory processes. Thus, it is thought, for example, that the ferryl radical (the hypothetical intermediate in lipoxygenase catalysis) damages the active sites of a number of enzymes, lipid membranes, DNA, etc. Although the mechanism of these processes is not known, AOS can apparently give rise to rearrangement of regions of the membrane, affect the transport of Ca^{2+} and the activation of phospholipases, and cause the release of eicosanoids, which in turn can produce a whole series of biochemical changes.

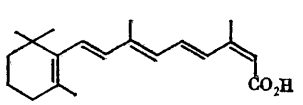
5. Certain other inhibitors

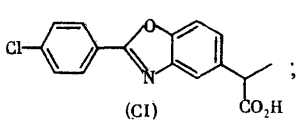
There are many compounds that inhibit LO (mainly 5-LO) for which the mechanism is not known and there is no reasonable theory for combining them into classes. There are also many individual reports about inhibitors which do not belong to any of the groups described above.

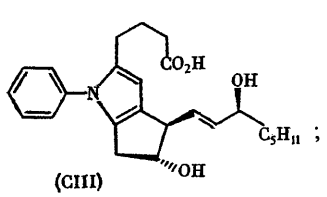
Thus, the ability of retinoids to inhibit 5-LO selectively has been established,[95] the most active being 13*Z*-retinoic acid (C).

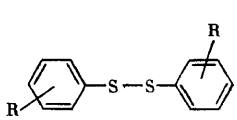
Benoxaprofen (CI), a non-steroid antiinflammatory drug used for the treatment of psoriasis, is a non-selective inhibitor of 5-LO whose mode of action is unclear.[96]

Aryl disulphides (CII), reported by research workers from Merck as a new class of selective inhibitors of 5-LO, are able to reduce the level of hydroperoxides needed for enzyme activation.[75,96,97]

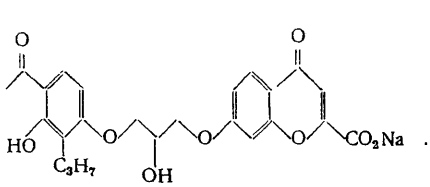

(C)


(CI)


(CIII)


(CII)

Compound U-60,257 (CIII) is an inhibitor which acts simultaneously at several points of the arachidonic acid pathway. Thus, it was described originally as an inhibitor of glutathione transferase. However, it was subsequently shown to have the ability to deactivate 5-LO and have the properties of a peptidoleukotriene antagonist.[98] Another active antagonist, SRS-A-FLP-55712 (CIV), which had already been adopted for medical use and was widely used for biochemical studies of the effects caused by LTC_4,[99] also proved to be an inhibitor of 5-LO (IC_{50} = 20 μM).[100]


(CIV)

An interesting example of an inhibitor that acts as a suicide substrate is phenylhydrazine (CV), which irreversibly deactivates soybean 15-LO.[101] It was established that deactivation is dependent on phenyldiazine (CVI) formed by autoxidation of phenylhydrazine:

$$\underset{\text{(CV)}}{PhNHNH_2} \xrightarrow[M^{n+}]{O_2} \underset{\text{(CVI)}}{RhN{=}NH} + H_2O_2, \quad (1)$$

$$\underset{\text{(CVI)}}{PhN{=}NH} + Fe\,(III) \rightarrow Ph^{\cdot} + N_2 + Fe\,(II). \quad (2)$$

The Fe(III)-enzyme is sensitive to phenyldiazine formed non-enzymatically according to Eqn. (1). However, deactivation is related not only to the conversion of the enzyme to a Fe(II)-containing inactive form, since excess 13*S*-HPOD does not cause the enzyme to be reactivated and the Fe(II)-enzyme is also irreversibly deactivated by phenylhydrazine.[101]

The activity exhibited by the haloethane 1,1,1-trifluoro-2-bromoethane is difficult to explain in terms of its structure. This compound (widely used in anaesthesia) suppresses the synthesis of leukotrienes and hydroxy acids by 5-LO in leucocytes.[102] Inhibition is reversible (removal of the inhibitor reactivates the enzyme) and depends on the dose. It was also established that this haloethane blocks the release of arachidonic acid from phospholipids and the synthesis of LTC_4 by glutathione transferase.[102] Its mode of action remains unclear, but it is evident that this compound acts at the second or even third stages of the enzymatic pathway.

Thus, the suppression of lipoxygenase activity may occur as a result of the effect of very different factors, which have still in part not received a rational explanation. Thus, it was established that the selective suppression of the 5-lipoxygenase activity of alveolar macrophages occurs during smoking.[103] Selective suppression only occurred for 5-lipoxygenase products (LT and 5-HETE) while TXB_2 and PGE_2 were formed in unchanged quantities. The mechanism of inhibition has not been established but it is thought to be related to the effect of free radicals generated by smoking on the active site of 5-LO.[103] However, this does not explain the selectivity of inhibition.

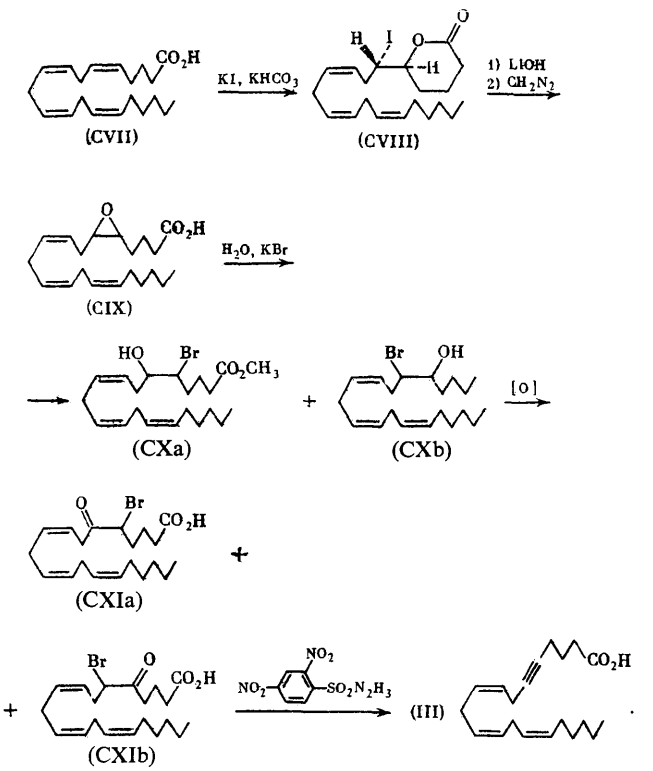
IV. The chemical synthesis of lipoxygenase inhibitors

The majority of the inhibitors of lipoxygenase oxidation of polyenoic acids examined are polyunsaturated systems containing double (separated by methylene groups, conjugated or cumulated) and triple bonds. Their synthesis is related, on the one hand, to the formation of a given carbon skeleton and, on the other hand, to the introduction (including during the build-up stage) of double bonds of a given configuration and triple bonds.

The following methods have been used to produce triple bonds in inhibitor molecules: 1) from the epoxide of the corresponding polyenoic acid;[67,104] 2) by condensing iodo- or bromo-allene with suitable lithium derivatives;[27,105] 3) by the reaction of metal acetylides with halogen derivatives.[106,107]

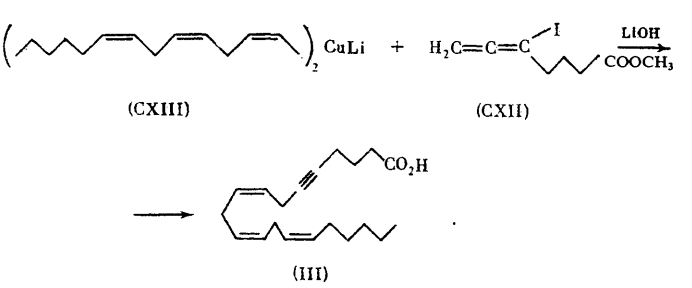
The application of these three approaches to the synthesis of acetylenic inhibitors can be conveniently examined in the case of 5,6-dehydroarachidonic acid.

Thus, the first synthesis of 5,6-DHA from arachidonic acid (CVII) was carried out by converting it to a lactone and then to epoxide (CIX) by the action of lithium hydroxide,[68] Epoxide (CIX) was converted to a mixture of isomeric bromohydrins (CXa, b) followed by a Jones oxidation to form a mixture of bromoketones (CXIa, b). Reaction of the isomeric mixture (CXIa, b) with 2,4-dinitrobenzene-sulphonyl hydrazone yielded the methyl ester of 5,6-DHA (IIIa):[67]

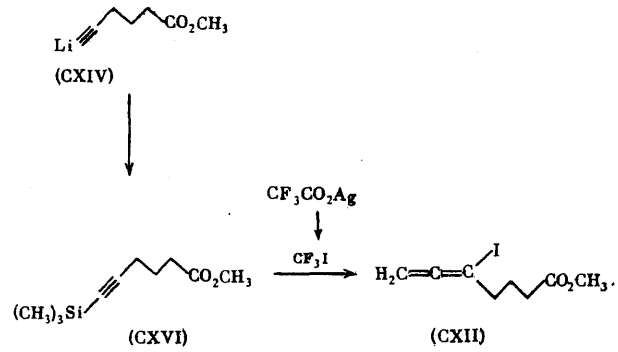


8,9-, 11,12-, and 14,15-DHA were obtained similarly via the respective epoxides.[67,108]

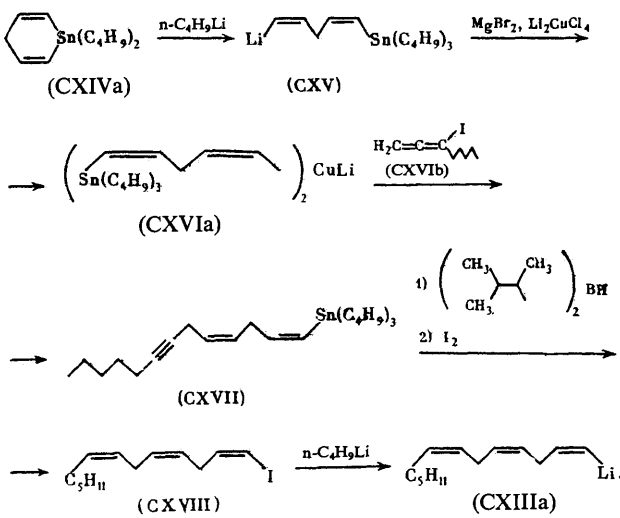
5,6-Dehydroarachidonic acid (III) may also be obtained by a complete synthesis, the key components of which are methyl 5-iodo-5,6-heptadienoate (CXII) and the lithium derivative of tridecatriene (CXIII):[27]



Iodoallene (CXII) is obtained by silylation of the lithium derivative of methyl 5-hexynoate (CXIV) with trimethylsilyl chloride in THF–HMPT followed by a reaction with silver trifluoroacetate in methylene chloride:

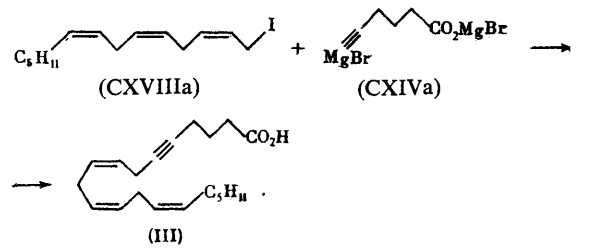


The synthesis of 1-lithio-1,4,7-tridecatriene (CXIII) is carried out by ring opening of 1,1,-di-n-butyl-1-stanna-2,5-cyclohexadiene (CXIVa) with n-butyllithium followed by extension of the carbon chain through the reaction of 1-lithio-5-tributylstannyl-1,4-pentadiene cuprate (CXVIa) with 3-iodo-1,2-octadiene (CXVIb), obtained in a similar manner to iodoallene (CXII):

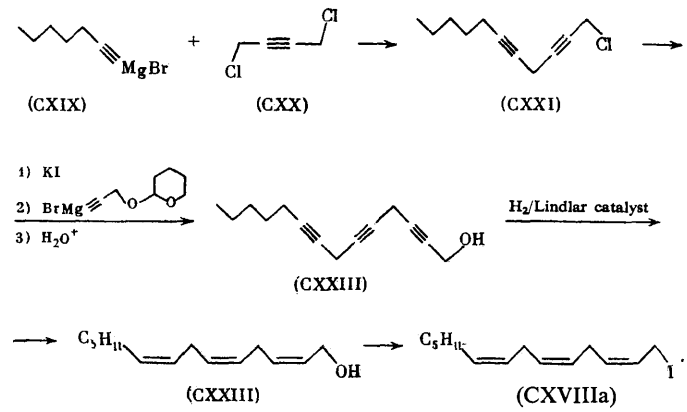


The triple bond in (CXVII) formed as a result is reduced with disiamylborane to a *cis*-double bond.[27]

The synthesis of 5,6-DHA from acetylenic compounds was achieved by cross-combining propargyl- and allyl-type halides (tosylates) with ω-acetylenic compounds.[107] 1-Iodo-2*Z*,5*Z*,8*Z*-tetradecatriene (CXVIIIa) and 5-hexynoic acid (CXIVa) were selected as the key synthons:

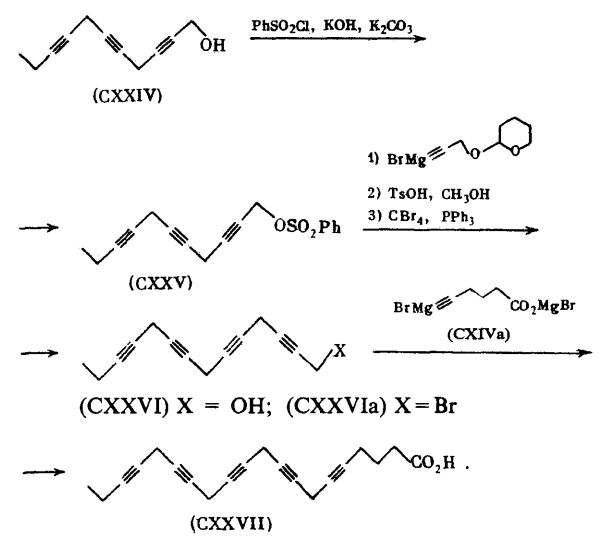


The triene iodide was synthesised by starting from 1-heptyne (CXIX), which was condensed with 1,4-dichlorobutyne (CXX) to give 1-chloro-2,5-undecadiyne (CXXXI):



Iodide (CXXIa), obtained from the diyne chloride (CXXI), was condensed with protected propargyl alcohol followed by removal of the protecting group and hydrogenation on a Lindlar catalyst. The triene alcohol (CXXIII) obtained in this manner was converted to the corresponding iodide (CXVIII) via the mesylate.

Another example of the successful application of a method for the preparation of eicosapolyynoic acids from acetylenic compounds is provided by a novel synthesis of 5,8,11,14,17-eicosapentaynoic acid (CXXVII)—a potential LO inhibitor.[108] The starting material for this was 2,5,8-undecatriynol (CXXIV),[109] conversion of which to the benzenesulphonate (CXXV) and condensation with the magnesium bromide derivative of protected propargyl alcohol gave 2,5,8,11-tetradecatetraynol (CXXVI). Subsequent replacement of the hydroxyl group in this compound by bromine gave 1-bromo-2,5,8,11-tetradecatetrayne (CXXVIa). The latter condensed with 5-hexynoic acid to form the required acid (CXXVII):



This type of approach to the synthesis of the pentaynoic acid (CXXVII) was also known previously,[110] but the use of propargyl halides to form polyacetylenic structures (in particular for the preparation of 5,8-nonadiynoic acid)[110] resulted in relatively low yields. Therefore, the tetrayne bromide (CXXVIa) and 5-hexynoic acid (CXIV) were selected by the authors as key components. The use of the benzenesulphonate (CXXV) instead of the corresponding bromide[111] made it possible to conduct the reaction under milder conditions (20 °C) and led to an increase in yield by 10–20%.

The double bonds in inhibitor molecules (both *cis*- and *trans*-) have been formed, as a rule, by means of the Wittig reaction.[35,36,38,39,48,82] Moreover, as has already been demonstrated, *Z*-double bonds may be obtained by the reduction of triple bonds on a Lindlar catalyst,[34,59,107] disiamylborane,[27] R1 or R2 nickel[112] (the use of the latter has only been reported for systems containing no more than two triple bonds).

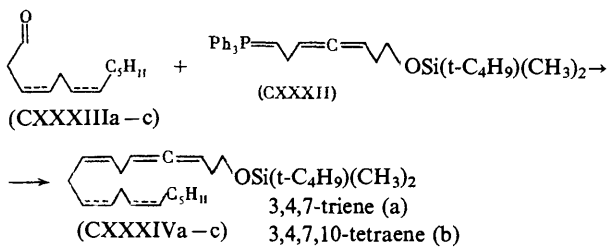
A significant disadvantage of the Wittig reaction is its low stereoselectivity.

The stereochemical result of the reaction is affected by the presence of lithium salts, which causes an increase in the proportion of *trans*-alkenes in the same reactions when the synthesis is conducted in non-polar solvents.[113] On the other hand, by using HMPT in the Wittig reaction it is possible to increase the proportion of the *cis*-isomer from 85 : 15 (*cis* : *trans*) to virtually pure *Z*.[54]

The Wittig reaction may be accompanied by side reactions, for example, isomerisation of the neighbouring double bond.[114] By using phosphonates (Wittig–Horner reaction) it is possible to improve the stereoselectivity of condensation slightly in favour of the formation of *trans*-alkenes. Attempts to increase the proportion of *Z*-products proved largely unsuccessful.[113,115,116]

Despite all these disadvantages the Wittig reaction remains the main method for forming double bonds in modified acid inhibitors (mainly the *Z*-configuration).[38,39,54]

Thus, the synthesis of 4,5-eicosaallenic acids is based on the stereoselective Wittig condensation of the allenic ylide (CXXXII) with the respective aldehyde (CXXXIIIa–c), the products of which are the nonadecasilyl ethers (CXXXIVa–c):[54]

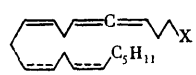


(CXXXIIIa–c) (CXXXII)

(CXXXIVa–c)

3,4,7-triene (a)
3,4,7,10-tetraene (b)
3,4,7,10,13-pentaene (c).

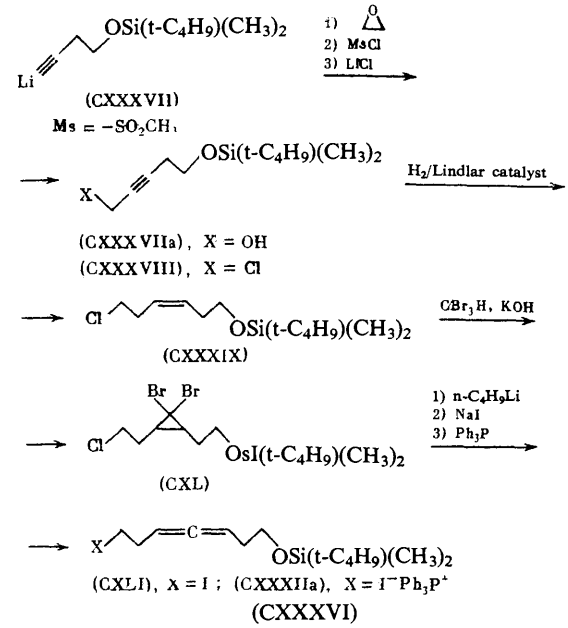
The subsequent conversion of the silyl ethers to bromides (CXXXVa–c) and the reaction of the Grignard reagents obtained from them with carbon dioxide gave 4,5-alleneicosanoic acids (IVa–c):



(CXXXVa–c) X = Br
3,4,7-triene (a)
3,4,7,10-tetraene (b)
3,4,7,10,13-pentaene (c)

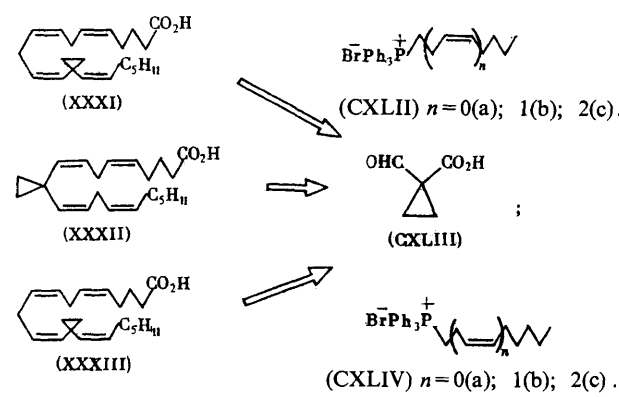
(IVa–c) X = CO_2H
8*Z*-eicosa-4,5,8-triene (a);
8*Z*,11*Z*-eicosa-4,5,8,11-tetraene (b);
8*Z*,11*Z*,14*Z*-eicosa-4,5,8,11,14-pentaene (c).

A common intermediate in the synthesis of allenic acids (IVa–c) is [7-(t-butyldimethylsilyloxy)-hepta-3,4-dien-1-yl]triphenylphosphonium iodide (CXXXVI), which was obtained from the lithium derivative of 3-butynyl t-butyldimethylsilyl ether (CXXXVII) by alkylation of the latter with ethylene oxide to form the monoprotected diol (CXXXVIIa), which was then converted to the chloride via the mesylate. Catalytic reduction of the triple bond of the chloride gave 6-chlorohexen-3*Z*-yl t-butyldimethylsilyl ether (CXXXIX), which was then converted to the corresponding dibromocyclopropane (CXL) by reaction with bromoform and potassium hydroxide in the presence of a phase-transfer catalyst. Conversion of the cyclopropane (CXL) to 1-chlorohepta-3,4-dien-6-yl t-butyldimethylsilyl ether (CXLI) by reaction with n-butyllithium and the subsequent replacement of chlorine by iodine and quaternisation led to the required component (CXXXVI):



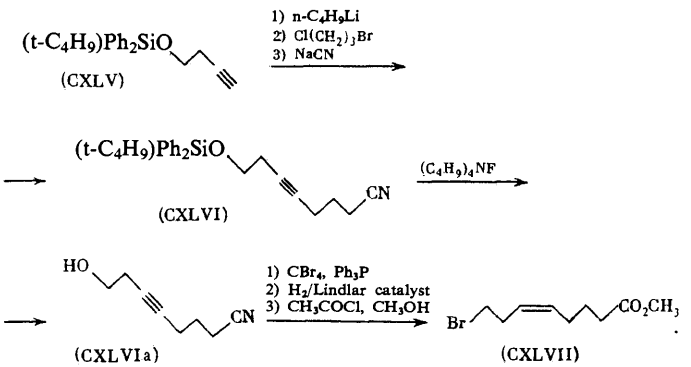
(CXXXVII)
Ms = $-SO_2CH_3$
(CXXXVIIa), X = OH
(CXXXVIII), X = Cl
(CXXXIX)
(CXL)
(CXLI), X = I ; (CXXXVIIa), X = $I^-Ph_3P^+$
(CXXXVI)

For a number of syntheses of polyenoic lipoxygenase inhibitors construction of the carbon skeleton using condensations of terminal acetylenic compounds with propargyl (allyl) halides (followed by selective reduction) as well as the formation of double bonds by the Wittig reaction is typical. This approach was used in the synthesis of the so-called ethanoarachidonic acids (XXXI)–(XXXIII).[38,39] Retrosynthetic analysis led Nicolaou et al.[38,39] to the phosphonium bromides (CXLIIa–c), (CXLIVa–c), and the cyclopropane derivative (CXLIII):

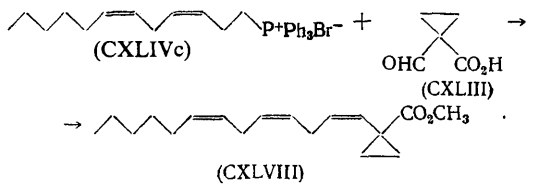


(XXXI) (CXLII) *n* = 0(a); 1(b); 2(c).
(XXXII) (CXLIII);
(XXXIII) (CXLIV) *n* = 0(a); 1(b); 2(c).

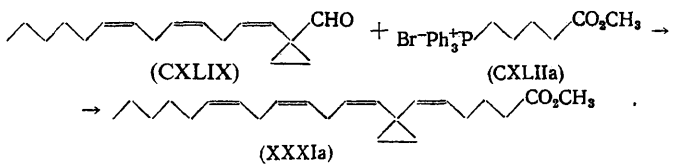
The synthesis of phosphonium salt (CXLIIb) was carried out by alkylation of the lithium derivative (CXLV) with chlorobromopropane followed by replacement of bromine by a cyano group, giving nitrile (CXLVI), which after desilylation, bromination, and reduction was converted to methyl ester (CXLVII)—the direct precursor of the required compound:



Phosphonium salts (CXLIVa–c), formed in a similar manner from the corresponding terminal alcohols, were used for subsequent condensation with the cyclopropane derivative (CXLIII):

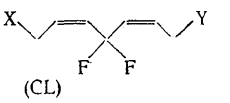


Subsequent conversion of methyl ester (CXLVIII) to an aldehyde and its condensation with phosphonium salt (CXLIIa) gave ethanoarachidonic acid (XXXI):



As has already been indicated, a versatile approach to the synthesis of methylene-separated polyene and polyenyne structures is a method which has already become established and the basic principles of which were previously developed by Osbond.[117] This method is based on the successive build-up of the carbon skeleton by condensation of magnesium halide derivatives of terminal acetylenic compounds with propargyl halides followed by reduction of the complete polyyne system or its individual parts. However, in a number of cases this method proves to be unacceptable despite the formal correspondence of the structure to what is required.

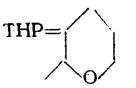
Thus, the synthesis of fluorine-containing analogues of arachidonic acid (XXII)–(XXV) is based on a substantially different approach to the formation of a methylene-separated polyene structure.[34,59] The starting point in this approach is formation of the difluoroallyl system (CL), which is carried out by means of a chain reaction involving an acetylene anion containing substituents X and CF_2ClBr:[34]



(CL)

X = OTHP, Y = OSi(t-C4H9)(CH3)2

$$\underset{\text{(CLI)}}{THPOCH_2C{\equiv}CLi} \xrightarrow[THF,\ -80\ ^\circ C]{CF_2ClBr} \underset{\text{(CLII), 52\%}}{THPOCH_2C{\equiv}CCF_2Br} + \underset{\text{(CLIII), 25\%}}{THPOCH_2C{=}CBr}.$$



(3)

The following mechanism for an ionic chain reaction has been proposed:[34,39]

$$\text{Initiation } Nu^- + BrCF_2Cl \rightarrow NuBr + CF_2Cl^-,$$

$$\text{Chain growth} \begin{cases} CF_2Cl^- \rightarrow :CF_2 + Cl^-, \\ Nu^- + :CF_2 \rightarrow NuCF_2^-, \\ NuCF_2^- + BrCF_2Cl \rightarrow NuCF_2Br + CF_2Cl^-, \end{cases}$$

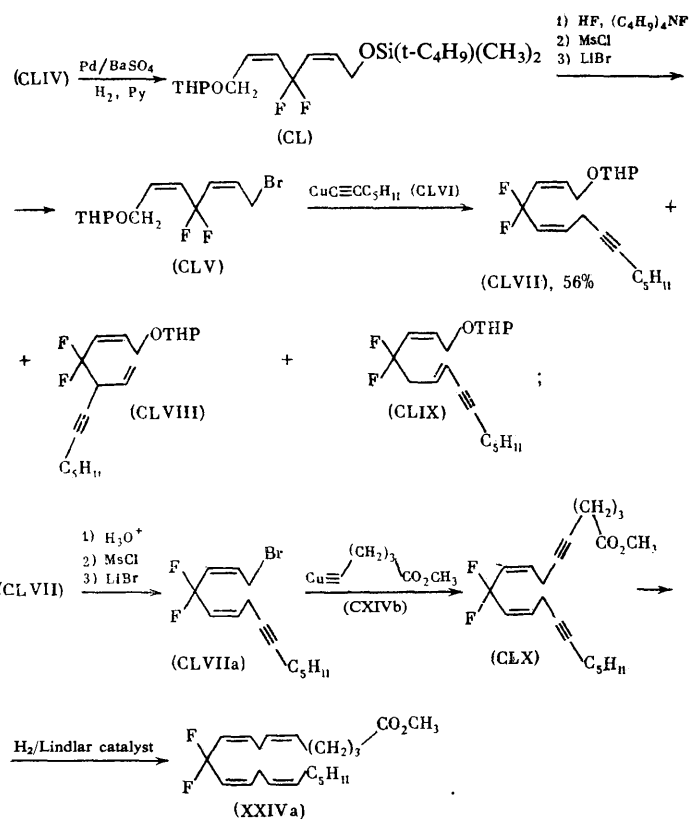
which is supported by the formation of bromide (CLIII) in reaction (3). By subsequently converting difluorobromide (CLII) to the corresponding iodide, it was possible to carry out a second condensation with acetylide anion as in (4), leading to the formation of the asymmetric difluorodiyne (CLIV):

$$\underset{\text{(CLIIa)}}{THPOCH_2C{\equiv}CCF_2I} + \underset{\text{(CLIa)}}{LiC{\equiv}CCH_2OSi(t\text{-}C_4H_9)(CH_3)_2} \rightarrow$$

$$\rightarrow \underset{\text{(CLIV)}}{THPOCH_2C{\equiv}CCF_2C{\equiv}CCH_2OSi(t\text{-}C_4H_9)(CH_3)_2}. \quad (4)$$

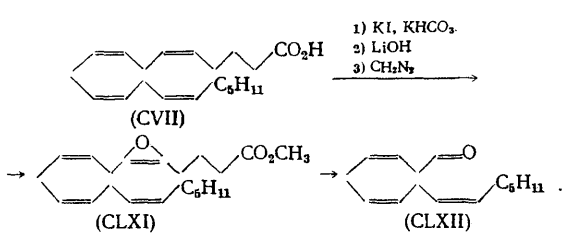
Reduction of difluorodiyne (CLIV) over $Pd-BaSO_4$ in pyridine yielded the key intermediate—difluoro-*Z*-diene (CL). After this there was the problem of forming two different carbon bonds with the respective substituents. This only proved possible with the use of cuprate reagents. Thus, condensation of the allyl bromide (CLV) with the heptynyl cuprate (CLVI) gave difluorodienyne (CLVII) (56% yield). There are different opinions in the literature about the possibility of using a diyne bromide (CLIVa) in a condensation.[34,118] The condensation is accompanied by the formation of branched (CLVIII) and conjugated (CLIX) enynes. Subsequent condensation with the cuprate of methyl hexynoate led to the dienyne (CLX),

which was hydrogenated on a Lindlar catalyst to give the required acid (XXIVa):[34]

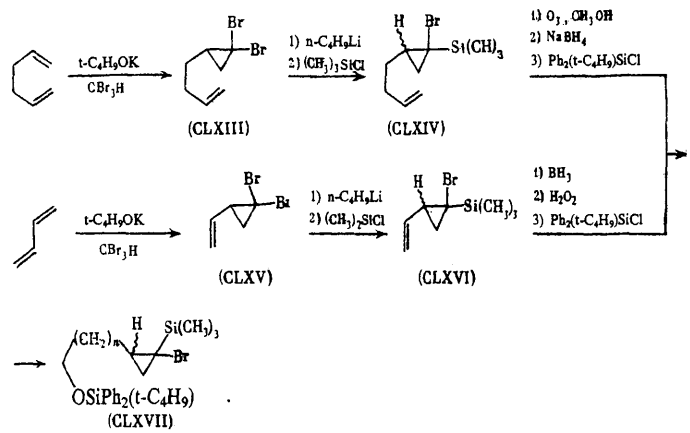


A widely used method for the synthesis of derivatives of arachidonic acid involves its direct conversion to the required compounds or the formation from it of separate residues of the final structures.

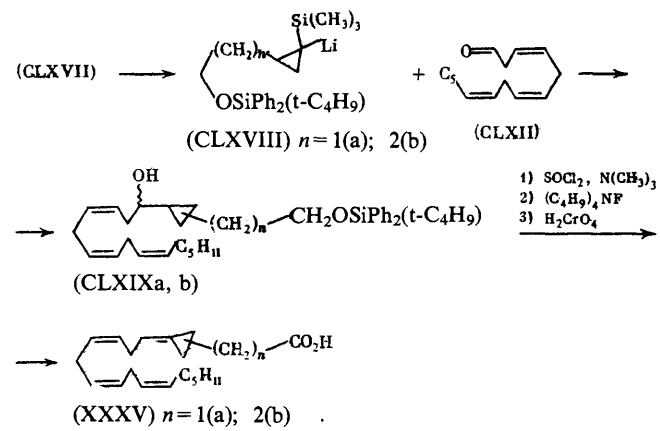
Thus the synthesis of methylenecyclopropane analogues of arachidonic acid[57] was achieved by iodolactonisation of the latter with subsequent conversion to an epoxide (in a similar manner to the approach of Corey et al.[67]) and its oxidation to an aldehyde:



The starting compounds in the synthesis of the methylenecyclopropane residue were 1,3-butadiene and 1,4-heptadiene:



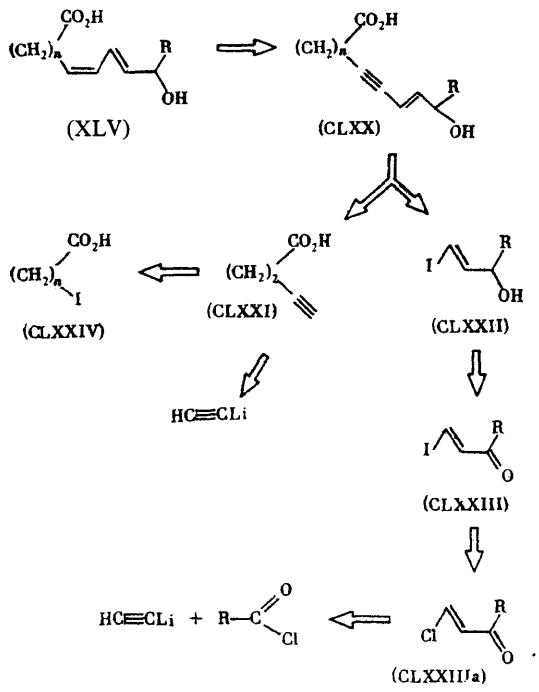
Metallation of (CLXVII) and reaction with aldehyde (CLXII) gave a mixture of four diastereomers (CLXVIIIa, b) which after chromatographic separation were converted to the silanes (CLXIXa, b). Desilylation and oxidation of the latter yielded the required acids (XXXVa) and (XXXVb):



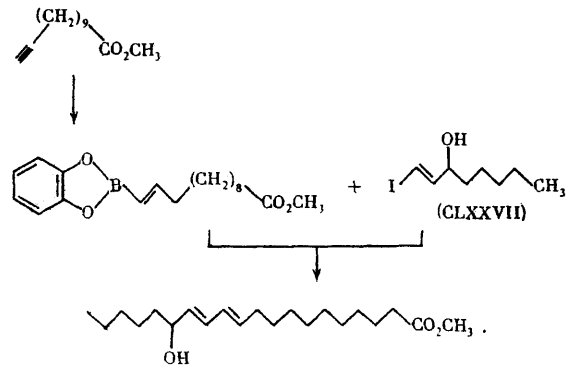
The synthesis of inhibitor analogues of lipoxygenase metabolites is carried out using similar synthetic methods.

Retrosynthetic analysis of 15-hydroxy-11*Z*-13*E*-dienoic acid (XLV) [64] shows that a reasonable method of building up this structure involves the condensation of ω-acetylenic acid (CLXXI)

with hydroxyvinyl halides to form the hydroxyenyne intermediates (CLXX), which are then reduced to the final (*Z*,*E*)-dienes:



Condensation was carried out by using tetrakis(triphenylphosphine)palladium(0) and cuprous iodide in triethylamine. By modifying the conditions it was possible to obtain the (*E*,*E*)-dienes, which were synthesised using 11*E*-carbomethoxy-1-undecylpyrocatechinborane (CLXXVI) and 3-hydroxy-1*E*-octenyl iodide (CLXXVII):



A detailed examination of the methods for synthesising inhibitors and antagonists with a different structure to that of the analogues of acid substrates and lipoxygenase metabolites (monocyclic and condensed heterocycles, phenol derivatives, etc.) is beyond the scope of the present review. These topics are covered in several publications.[119–124]

V. Conclusion

It is clear from the information given in this review that a large number of effective lipoxygenase inhibitors and antagonists of the corresponding metabolites with different chemical structures have been developed up to the present time. However, only a few of them have been used as antiallergic and antiinflammatory drugs;[7,50,93,125] without exception, all of these compounds in terms of their structure are far removed from lipoxygenase substrates and metabolites.

Heterocyclic lipoxygenase inhibitors acting as antioxidants, chelating agents of Fe(III) and via other, often undetermined mechanisms[7,88,90,91,129] have become quite widespread. A number of compounds that have been isolated from plants and microorganisms belong to this group.[126–128]

The synthesis of analogues of the precursor acids of eicosanoids is a promising trend for the development of compounds with antilipoxygenase activity, even though they are generally inactive *in vivo* and cannot be used as drugs. Compounds of this type can be used for a detailed study of the mechanism of conversion of eicosapolyenoic acids by LO and for obtaining information about the nature of groups forming part of the active site.[25,31,32,54]

Special mention should be made concerning inhibitors that do not have direct structural similarities with natural lipoxygenase substrates but with a good isosteric correspondence to the active site of the enzyme, which have been developed with the aid of three-dimensional computer models.[64,65,79]

Antagonists of lipoxygenase metabolites constitute an important independent group of antilipoxygenase compounds whose activity is determined by their ability to block the receptor interactions of eicosanoids.[40–43,72,73,112,123]

Thus, the problem of pharmacological regulation of the arachidonic acid pathway and its lipoxygenase metabolism in particular is an extremely complex, multilevel question and may be resolved only by the continuation of studies in all the existing areas of research into fundamentally new antilipoxygenase agents and factors as well as combining the separate research efforts on the basis of a common approach.

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Selective replacement of hydrogen at a saturated carbon atom under the action of oxidising agents

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ABSTRACT. Data have been correlated for the heterolytic substitution reaction of hydrogen atoms in saturated hydrocarbons and also in some ethers and esters under the action of oxidising agents, viz. halogens, nitronium salts, halogen fluorides and ozone. Alternative schemes of electrophilic and nucleophilic substitution of hydrogen at an sp^3-hybrid carbon atom are considered.

The bibliography contains 79 references.

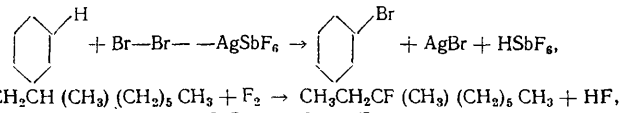
Contents

I. Introduction 501
II. Reactions of saturated hydrocarbons in Hal_2–Lewis acid (Hal = Br, Cl) systems and other oxidising agents 502
III. Heterolytic oxidation of ethers 504
IV. Selective fluorination of organic compounds containing tertiary and secondary hydrogen atoms by elementary fluorine and halogen fluorides 505
V. Reactions of saturated organic compounds with ozone 508
VI. General rules and mechanism for the oxidative replacement of a hydrogen atom at a saturated carbon atom 510

I. Introduction

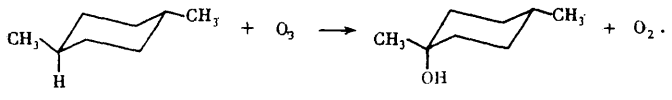
It was shown recently that halogen atoms in alkyl halides are selectively substituted by other functional groups under the action of various oxidising agents with the formation of extremely valuable final products. Proof has been presented of the fact that all these reactions are linked by a general mechanism and may be considered as oxidative nucleophilic substitutions of halogen at a saturated carbon atom.[1]

In recent years it has been reported that similar oxidising agents are capable of selectively replacing hydrogen atoms (mainly at tertiary carbon atoms or α-hydrogen atoms in ethers). Typical examples of such reactions are:



$$CH_3CH_2CH(CH_3)(CH_2)_5CH_3 + F_2 \rightarrow CH_3CH_2CF(CH_3)(CH_2)_5CH_3 + HF,$$

$$(CH_3)_2CHCO_2R_F + BrF_3 \rightarrow (CH_3)_2CFCO_2R_F + HF + Br_2,$$



Many investigators of these reactions have considered the development of preparative methods of 'functionalising' organic compounds by replacement of hydrogen at a saturated carbon atom to be an extremely promising direction and the selection of conditions at which the yield of substitution product reaches 50–60% to be a great success. Since low temperature non-radical oxidative substitution processes for hydrogen atoms are a very important type of chemical conversion of organic compounds and are seemingly fairly widely distributed in nature, it seemed expedient to us just now to correlate all the available information on such processes. We are confident that analysis of such data will permit formulation of a fairly objective representation of the overall rules of oxidative substitution of hydrogen atoms and planning of routes for further investigation of the problem.

Table 1. Halogenation of alkanes by molecular halogen in the presence of Lewis acids in CH_2Cl_2.[9,10]

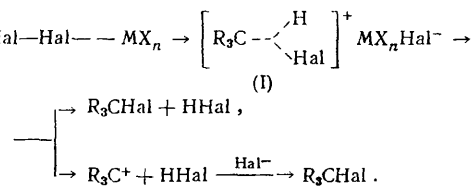
No.	Alkane	Halogen	Lewis acid	Molar ratio Hal:Lewis acid:alkane	Temp. °C (time, min)	Reaction products (yield[a], %)
1	Isobutane	Cl_2	$AlCl_3$[b]	1:0.1:1	25 (960)	over 20 products[c]
2	Isobutane	Cl_2	$AgSbF_6$	0.5:0.1:1	−15 (10)	t-butyl chloride (7)
3	Isobutane	Br	$AgSbF_6$	0.5:0.1:1	−15 (10)	isobutyl bromide (84) t-butyl bromide (11) 2,3-dibromoisobutane (6)
4	Cyclohexane	Cl_2	$AgSbF_6$	0.5:0.1:1	15 (10)	cyclohexyl chloride (5)
5	Cyclohexane	Br_2	$AgSbF_6$	0.5:0.1:1	25 (15)	cyclohexyl bromide (27)
6	Norbornane	Cl_2	$AlCl_3$	1:0.1:1	25 (960)	*exo*-2-chloronorbornane (17) *endo*-2-chloronorbornane (8) 7-chloronorbornane (4)
7	Norbornane	Br_2	$AgSbF_6$	0.5:0.1:1	25 (15)	*exo*-2-bromonorbornane (71) *endo*-2-bromonorbornane (12) 7-bromonorbornane (12)
8	Adamantane	Cl_2	$AlCl_3$	1:0.1:1	25 (1260)	1-chloroadamantane (63) 2-chloroadamantane (3)
9	Adamantane	Cl_2	$AgSbF_6$	0.5–0.1:1	−45 (5)	1-chloroadamantane (62) 2-chloroadamantane (1) 1-hydroxyadamantane (36)

[a] In the case of $AlCl_3$ catalyst the yield is given on Cl_2 taken, in the case of $AgSbF_6$ on catalyst.
[b] Reactions were carried out without solvent.
[c] t-Butyl chloride and isobutyl chloride were absent from the products.

The numerous reactions for the oxidation of hydrocarbons by transition metal salts and by chromic and manganic acids are not considered in the review. The ample material on this type of side-chain oxidation of alkylaromatic compounds is correlated in a review paper[2] and in a monograph.[3] Preparative possibilities and proposed mechanisms of oxidation of saturated hydrocarbons by chromic acid and by transition metal salts have been described.[4–7]

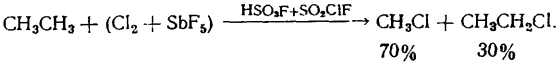
II. Reactions of saturated hydrocarbons with Hal_2–Lewis acid (Hal = Br, Cl) systems and other oxidising agents

The first attempts to effect the preparative replacement of hydrogen atoms at a saturated carbon atom by electrophilic oxidising agents under conditions excluding the possibility of free radical reactions were undertaken by G Olah in the seventies.[8–10] It was shown that Cl_2 and Br_2 in the presence of SbF_5, $AlCl_3$ and $AgSbF_6$ were able to interact at low temperature in the dark with saturated hydrocarbons to form alkyl halides (Table 1). He proposed that positively polarised halogen effected a frontal electrophilic attack on the C–H bond forming a pentacoordinate carbenium ion (I) which may then be converted into an alkyl halide by two routes: first, by ejection of a proton and formation of a bond between the carbon atom and the attacking halogen atom or second, by transfer of a hydride ion to the oxidising agent with subsequent capture of the resulting carbocation by halide anion.

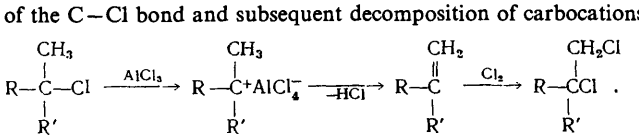


(I)

The use of antimony pentafluoride, the most powerful chlorination catalyst, in chlorination reactions led not only to hydrogen atom replacement (chlorination) but also to cleavage of a σ C–C bond in the alkane (chlorolysis). Thus the reaction of ethane in the Cl–SbF_5 system at room temperature gave methyl chloride and ethyl chloride in the ratio 70:30

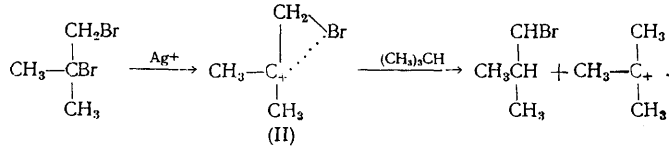


In the presence of the weaker catalysts $AlCl_3$ and $AgSbF_6$ no chlorolysis was observed. All types of σ C–H bonds (primary, secondary, tertiary) were chlorinated on catalysis by aluminium chloride, in addition the resulting alkyl halides were converted into products of further chlorination as a result of the ease of heterolysis of the C–Cl bond and subsequent decomposition of carbocations.



Thus isobutane gave more than 20 products in the presence of $AlCl_3$ (Table 1, compound No. 1). Since the elimination of a proton and double bond formation at a bridgehead is impossible for norbornane and adamantane, the chlorination of these compounds gave appreciable quantities of the corresponding monochlorides (Table 1, compounds No. 6, 8).

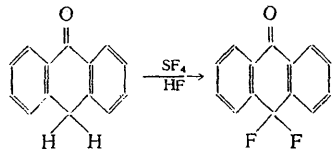
The Hal_2–$AgSbF_6$ systems possess even lower electrophilicity and correspondingly greater selectivity towards the C–H bond. Only isoalkanes and cyclic hydrocarbons (see Table 1) react in these systems at low temperature. In the presence of $AgSbF_6$, alkyl chlorides are less inclined to further conversion than with aluminium chloride. Thus only t-butyl chloride is formed from isobutane (Table 1, No. 2). In contrast to chlorination the bromination of isobutane gave isobutyl bromide, t-butyl bromide and 2,3-dibromobutane (Table 1, No. 3). The fact that the main bromination product of isobutane is not t-butyl bromide but isobutyl bromide is explained by transfer of a hydride ion from isobutane to the carbocation (II) which was formed by heterolysis of the tertiary C–Br bond in 2,3-dibromobutane:



(II)

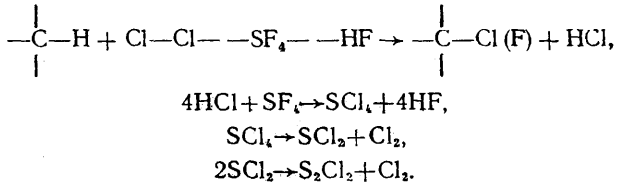
This was confirmed by special experiments on the bromination of a mixture of 2,3-dibromobutane and isobutane in the presence of $AgSbF_6$.

Interesting communications have appeared recently on the influence of small additions of Cl_2 on the ability of SF_4–HF systems to replace hydrogen at a saturated carbon atom by fluorine.[11,12] It was known previously that these systems replace hydrogen atoms in anthrone and adamantane by fluorine at moderate temperatures (60–70 °C):[13,14]

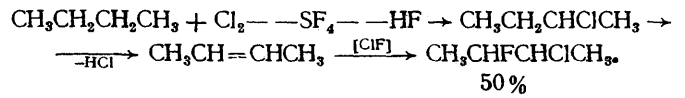


85%

It was shown[11] that after careful purification from traces of Cl_2 and SCl_2 (the initial product in SF_4 synthesis) sulphur tetrafluoride was unable to replace hydrogen in adamantane. Consequently it was concluded that Cl_2 was a necessary component of this system but the effectiveness of the action of traces of sulphur chlorides is linked with the generation of molecular chlorine in this system by the reaction sequence:[12]



On introducing large quantities of chlorine into the SF_4–HF system (molar component ratios 2:1:5 respectively) it was possible to effect substitution of hydrogen in n-butane even at 20 °C. The following reaction sequence was proposed to explain the observed facts:[12,15]

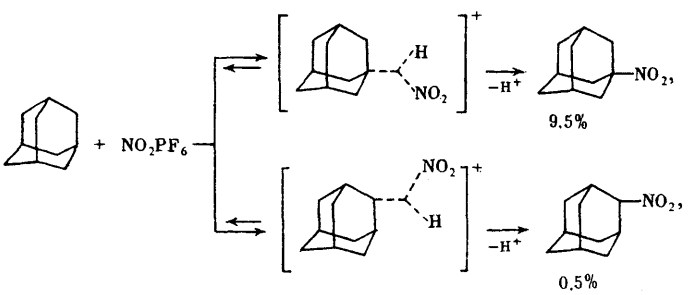


50%

However such an explanation is unconvincing since it is not very likely that dehydrochlorination of 2-chlorobutane may occur under these conditions. It is possible that alkenes are formed by loss of a proton from the intermediate carbenium ion resulting in transfer of hydride ion to the oxidising agent.

$$CH_3CH_2CH_2CH_3 + Cl_2 - - SF_4 - - HF \rightarrow [CH_3CH_2\overset{+}{C}HCH_3] \xrightarrow[-HCl]{} CH_3CH{=}CHCH_3 \xrightarrow{[ClF]} CH_3CHFCHClCH_3.$$

Oxidative replacement of hydrogen atoms in alkanes may be effected by various systems containing the nitronium cations.[16–19] On reaction of nitronium hexafluorophosphate with saturated hydrocarbons in an aprotic solvent at 25 °C nitroalkanes are formed although fission of σ C–C bonds has also been observed in addition to replacement of hydrogen atoms.[16] The yield of nitroalkanes in these reactions is extemely low, in the case of acyclic compounds the yield of products did not exceed 2–5%. The best result was obtained in the reaction of adamantane when 1- and 2-nitroadamantanes were isolated in 10% total yield.



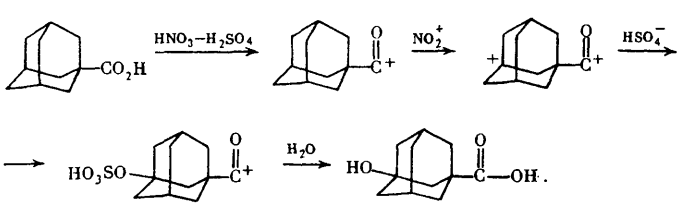
In the authors' opinion the main obstacle to achieving preparative yields is the high basicity of the solvent, containing atoms with unshared electron pairs, in comparison with the basicity of the σ C–H bond. A mixture of concentrated nitric and sulphuric acids may be used in place of nitronium salts in nitration reactions.[16] On nitrating isobutane with this mixture the following set of products was obtained: CH_3NO_2 (28%), $CH_3CH_2NO_2$ (5%), $(CH_3)_2CHNO_2$ (1%), $(CH_3)_3CNO_2$ (66%).

However carrying out the reaction in a mixture of strong acids was complicated by protolytic cleavage of the secondary and tertiary nitroalkanes.

$$(CH_3)_3CNO_2 \overset{H^+}{\rightleftarrows} (CH_3)_3CNO_2H^+ \rightarrow (CH_3)_3C^+ + HNO_2.$$

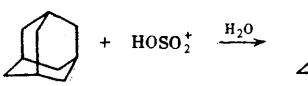
The interaction of 1-nitro-2,2-dimethylpropane with benzene and toluene in the presence of strong acids led only to the t-butyl derivatives of benzene and toluene.

On reacting 1-adamantanecarboxylic acid with a mixture of nitric and sulphuric acids no nitro derivatives were detected but 3-hydroxy-1-adamantanecarboxylic acid was obtained in high yield.[17] The authors proposed a reaction scheme including removal of the hydride ion by the nitronium cation with subsequent capture of the resulting carbocation by the hydrogen sulphate anion.



Analogous replacement of a hydrogen atom occurred on reaction of adamantane with 90–100% nitric acid and mixtures of it with acetic anhydride[18,19] or a mixture of 96–98% sulphuric acid with trifluoroacetic anhydride.[20] Thus on reacting adamantane with 90% HNO_3 the nitrate of 1-hydroxyadamantane was obtained in 50–65% yield.[18] It was proposed that in a $H_2SO_4/(CF_3CO)_2O$ mixture the active species is the $HOSO_2^+$ cation.[20] SO_2 is separated in the oxidation process.

$$H_2SO_4 + (CF_3CO)_2O \rightleftarrows HOSO_2^+ + CF_3CO_2^- + CF_3CO_2H,$$



$$H_2SO_3 \longrightarrow SO_2 + H_2O.$$

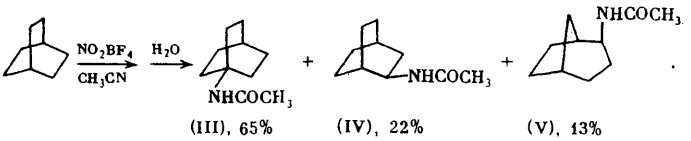
Evidently the oxidation of hydrocarbons by concentrated sulphuric acid occurs in a similar manner:[7]

$$RH + H_2SO_4 \rightarrow [R^+HSO_4^-] + SO_2 + H_2O.$$

On oxidation of adamantane with nitronium salts the magnitude of the kinetic isotope effect was 1.86,[21] of isobutane with a mixture of nitric and sulphuric acids 2,[22] and of 1,3,5-trimethyladamantane 4.4.[18] The kinetics of the oxidation of adamantane, and its derivatives substituted in the angular positions, by nitric acid in methylene chloride solution have been investigated.[23] It was established that the rate constants were linked linearly to the rate constants for solvolysis of the corresponding bromo derivatives and to the Taft induction constants. This is also in agreement with a mechanism including as limiting stage the removal of a hydride ion by the oxidising agent with the formation of the adamantyl cation. Evidence in favour of the mechanism involving the formation of carbenium ions was obtained not only in the oxidation of adamantane but also of other saturated organic compounds.[21,24] Thus on oxidation of 2-methylbutane with nitronium fluoroborate in acetonitrile at room temperature 2-acetamido-2-methyl-3-nitrobutane was obtained in good yield. Since this compound is also obtained by the addition of nitronium fluoroborate to trimethylethylene in acetonitrile medium the reaction sequence depicted in the scheme may be the sole explanation:

$$(CH_3)_2CHCH_2CH_3 \xrightarrow{NO_2BF_4} (CH_3)_2\overset{+}{C}CH_2CH_3 \xrightarrow{-H^+} (CH_3)_2C{=}CHCH_3 \xrightarrow[CH_3CN]{NO_2BF_4} (CH_3)_2CCHNO_2CH_3 \xrightarrow{H_2O}$$
$$\rightarrow (CH_3)_2CCHNO_2CH_3.$$
$$\quad NHCOCH_3$$

The interaction of bicyclo[2.2.2]octane with nitronium fluoroborate led to the formation of a mixture of acetamides (III–V) in 73% total yield.



(III), 65% (IV), 22% (V), 13%

The ratio of unrearranged acetamide (IV) to rearranged amide (V) was close to 2:1 as in the solvolysis of bicyclo[2.2.2]octyl bromobenzenesulphonate.[25] On oxidation of adamantane under

these conditions N-(1-adamantyl)acetamide (88%) was obtained. Norbornane gave exclusively N-(*exo*-2-norbornyl)acetamide (78%). The ease of transfer of hydride ions from adamantane, bicyclo[2.2.2]octane and norbornane was in direct relation to the stability of the corresponding carbenium ions.[26] Proof of the fact that nitro derivatives are not formed as intermediates on reaction of alkanes with nitronium fluoroborate in acetonitrile was the inertness of 2-methyl-2-nitropropane and 1-nitroadamantane towards the reagent at 25 °C.[21]

Trifluoroacetyl nitrate formed *in situ* in the reaction of ammonium nitrate and trifluoroacetic anhydride is also an efficient oxidising agent for saturated hydrocarbons:[24]

$$NH_4NO_3 + (CF_3CO)_2O \rightleftarrows CF_3CO_2NO_2 + CF_3CO_2NH_4.$$

Oxidation was carried out in trifluoroacetic acid medium at 25–40 °C. It was proposed that the active electrophile in this system was protonated trifluoroacetyl nitrate $[CF_3CO_2NO_2H]^+$. Under these conditions cyclooctyl trifluoroacetate was obtained in good yield (50%) from cyclooctane and also *exo*-2-trifluoroacetoxynorbornane (52%) and *exo*-2-norbornyl nitrate (23%) from norbornane.

III. Heterolytic oxidation of ethers

The α-hydrogen atoms of amyl ethers are replaced significantly more readily than hydrogen atoms in alkanes since the ether oxygen atom facilitates both the radical and ionic replacement of α-hydrogen atoms while stabilising the resulting free radical or carbocation intermediate.[27] Oxidation proceeds according to a free radical or ionic mechanism depending on the type of oxidising agent and on the conditions of carrying out the reaction. The classical oxidation reaction of ethers by atmospheric oxygen has been well studied and its free radical mechanism is not in doubt. On UV irradiation and also at elevated or room temperatures many alkyl ethers interact energetically with elementary chlorine by a free radical mechanism.[27,28] However dark low-temperature halogenation of ethers evidently proceeds according to a heterolytic mechanism and leads to replacement of hydrogen atoms by chlorine exclusively at the position α to the alkoxy group.[28–30] α-Chloroethyl ether (42%) and α,α′-dichlorodiethyl ether (57%) are obtained as a result of the chlorination of diethyl ether at –20 to –30 °C. But even at –5 to +5 °C more extensive chlorination occurs principally at the β-position.[28]

Due to the fact that the alkoxy group effectively stabilises carbenium ions, attack by the oxidising agent at the σ-bond of the α-hydrogen atoms leads to transfer of hydride ion to the oxidising agent with the formation of resonance-stabilised carbocation (VI):[27,29]

$$Hal{-}Hal + H{-}\underset{|}{\overset{|}{C}}{-}OR \rightarrow Hal^- + $$

$$+ HalH + \left[\underset{|}{\overset{|}{C}}{=}\overset{+}{O}R \;\; (VI)\right] \xrightarrow{Hal^-} Hal{-}\underset{|}{\overset{|}{C}}{-}OR,$$

Hal=Cl, Br.

Probably other oxidising agents may react under milder conditions with ethers by the same mechanism. Chlorine monofluoride is a reagent for which all descriptions of reaction with organic compounds bear a clearly marked heterolytic character.[12] At low temperature in HF medium it readily replaces an α-hydrogen atom in the ethyl group of 1-chloro-2,2-difluoro-3-oxapentane:[30]

$$CH_2ClCF_2OCH_2CH_3 + ClF \rightarrow CH_2ClCF_2OCHFCH_3.$$

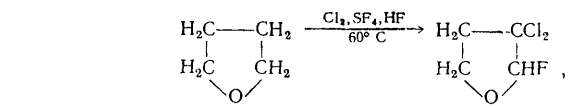
Bromine trifluoride at room temperature in the absence of solvent replaces a hydrogen atom in the methyl group of ether (VII) and an α-hydrogen atom in the ethyl group of compound (VIII):[31]

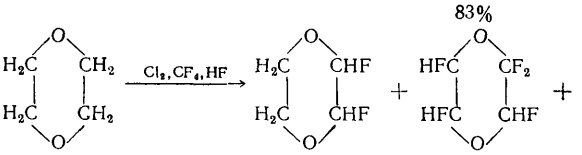
$$\underset{(VII)}{(CF_3)_2CHCF_2OCH_3} \xrightarrow[20°C]{BrF_3} \underset{48\%}{(CF_3)_2CHCF_2OCH_2F},$$

$$\underset{(VIII)}{(CF_3)_2CHCF_2OCH_2CH_3} \xrightarrow{BrF_3} \underset{74\%}{(CF_3)_2CHCF_2OCHFCH_3}.$$

Since the electron-donating ability of the oxygen atom is strongly reduced in a polyhalogenated alkoxy group, the ionic and radical halogenation of ethers of type (VII, VIII) proceeds with difficulty. Thus radical chlorination of similar compounds occurs only on UV irradiation. The use of such powerful electrophilic oxidising agents as ClF and BrF_3 permits heterolytic replacement of α-hydrogen atoms. The system Cl_2-SF_4-HF effectively fluorinates ethers at moderate temperatures.[6,10,14] In this way more extensive halogenation occurs, viz. replacement of β-hydrogen atoms predominantly by chlorine:

$$CH_3CH_2OCH_2CH_3 \xrightarrow[50°C]{Cl_2,SF_4,HF} \underset{89\%}{CCl_3CHFOCH_2CH_3},$$

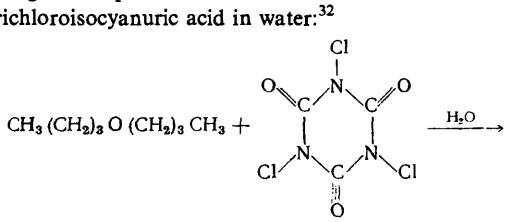




+ $CF_3CHFOCH_2CH_2F$.

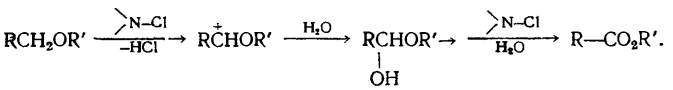
These reactions probably occur by the initial oxidative replacement of α-hydrogen atoms by fluorine according to a heterolytic mechanism analogous to that presented above. However as a result of the extreme instability of α-fluoroethers[28] the products of mild monofluorination are not isolated. Under more forcing conditions further fluorination and chlorination of the α-fluoroethers occur. The polyhalogenated ethers obtained in this way are then completely stable since the nucleophilic replacement of α-fluoro atoms occurs with more difficulty as a result of the electron-accepting influence of the vicinal halogens.

One further interesting example of the selective replacement of α-hydrogen atoms in ethers under the action of oxidising agents containing electropositive chlorine is the reaction of dibutyl ether with trichloroisocyanuric acid in water:[32]

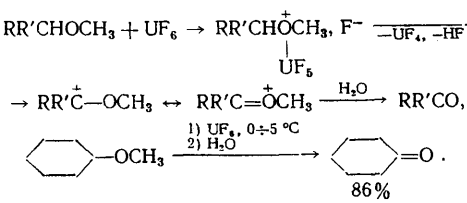


→ $CH_3(CH_2)_2CO_2(CH_2)_3CH_3$.

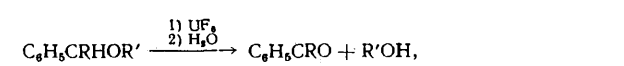
This reaction may be represented as follows:



Uranium hexafluoride has been proposed for the selective oxidation of ethers and certain other organic compounds.[33] Carbonyl compounds and alcohols are formed as a result of the oxidation of unsymmetrical ethers. In the case of methyl ethers the reaction proceeds regioselectively. The authors put forward a scheme assuming initial attack of uranium hexafluoride at the oxygen atom:

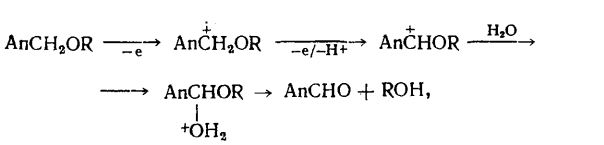


Aromatic compounds and aliphatic alcohols are formed on oxidation of alkyl benzyl ethers and benzhydryl ethers:



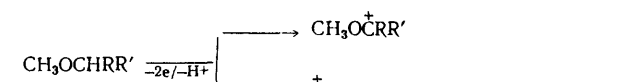
R = H or C_6H_5; R′ = alkyl, cycloalkyl.

It is interesting that extremely similar results were obtained on electrochemical oxidation of alkyl benzyl ethers.[34,35] An especially good yield (74 to 98%) was observed in the case of *p*-methoxybenzyl ethers. A mechanism was proposed for these reactions.[36]



An = anisyl.

By electrochemical oxidation of ethers it is possible to obtain orthoesters, acetates of hemiacetals or acetals which are readily hydrolysed in aqueous acidic medium and give the corresponding aldehydes in good yield.[34,37,38] The regioselectivity on electrochemical oxidation is the same as on oxidation by uranium hexafluoride and is determined by the ability of substituents at the reaction centre to stabilise the positive charge formed by elimination of the α-hydrogen atom:



R = H, alkyl; R′ = alkyl.

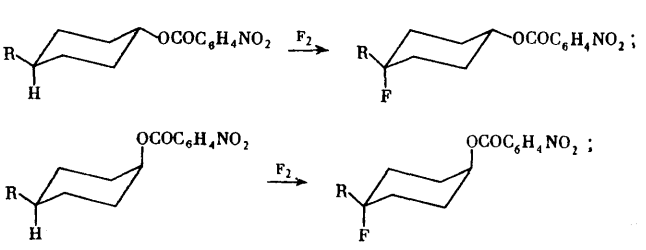
Consequently the hydrogen atoms of CH_3 groups are not affected during oxidation of mixed alkyl methyl ethers. For the same reason selective replacement of benzylic hydrogen atoms occurs for alkyl benzyl ethers having no electron-accepting substituents in the aromatic ring.[33,38]

IV. Selective fluorination of organic compounds containing tertiary and secondary hydrogen atoms, with elementary fluorine and halogen fluorides

Elementary fluorine reacts vigorously with organic compounds under the usual conditions which frequently leads to destruction of the hydrocarbon skeleton.[39] During the last 10 years Rozen and co-workers have developed preparative methods of replacing tertiary hydrogen atoms by fluorine using low temperature fluorination with elementary fluorine.[40–48] Fluorination was effected by passing a gaseous mixture of F_2 and N_2 containing 1 to 10% fluorine through a strongly diluted (0.1–0.3%) solution of the substrate in a mixture of $CFCl_3$–$CHCl_3$ (1:1) at –75 to –78 °C. Chloroform was a necessary component of the solvent, in Freon alone fluorination did not take place.[46]

Exhaustive data on fluorination by this means including literature since 1985 have been presented in a review.[49] We will give only the most typical examples illustrating the possibilities of this method.

Best results (70–90% yield) were obtained for cyclic hydrocarbons (Table 2, compounds 2–6). Evidently these results are not explained by their hydrogen atoms reacting more readily with F_2 but by the greater stability of such alkyl fluorides compared with acyclic fluorides. A special feature characteristic of oxidative fluorination is the possibility of replacing the hydrogen atom at position 1 of the norbornane system (Table 2, compounds 7, 8) in which the formation of carbenium ions is extremely disfavoured. 1-Fluorocamphane and 2-(1-norbornyl)ethyl acetate were obtained in low yield (15–20%). Electron-accepting substituents hampered replacement, consequently tertiary hydrogen atoms furthest removed from such substituents were replaced more readily. Thus a better result was obtained with a steroid diol diacetate than with the ditrifluoroacetate (Table 2, compounds 9, 10), in both cases the hydrogen atom replaced was that located furthest from the acceptors. Similarly the tertiary hydrogen atom in the position γ to the ester group was replaced in better yield than that in the β position (Table 2, compounds 11, 12). The presence of two electron-accepting substituents in the position β to hydrogen hindered replacement so much that the yield of the corresponding fluoride was extremely low (Table 2, compound 13). The stereochemistry of replacement of tertiary hydrogen atoms by fluorine in cyclohexane derivatives has been investigated.[47] Replacement occurred with retention of configuration in all cases.



R = CH_3, $(CH_3)_3C$.

On fluorinating bicyclo[2.2.2]octane by this method a rearrangement

was observed typical of a reaction proceeding with the formation of carbenium ions.[48]

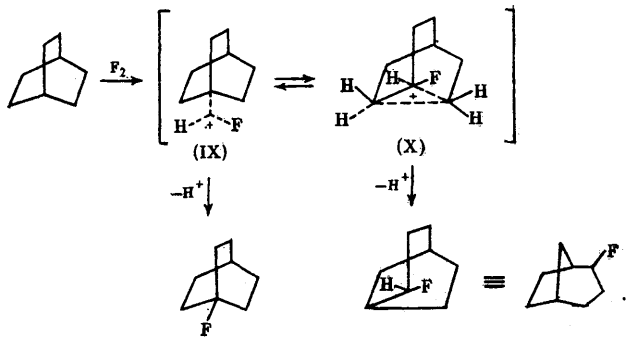
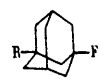
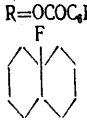
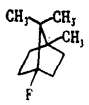
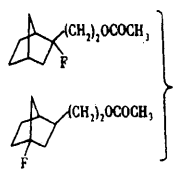
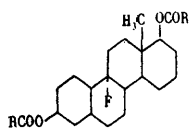
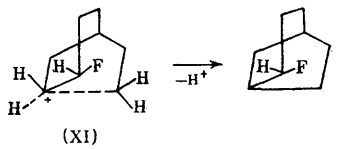


Table 2. Replacement of tertiary hydrogen atoms by fluorine using molecular fluorine in $CFCl_3-CHCl_3$ medium[a].

No.	Product[b]	Yield, %[c]	Refs.
1	$CH_3CH_2CH(CH_3)(CH_2)_6CH_3$	65	[47]
			
2	R=H	70	[40]
3	R=NHCOCF$_3$	83	[40]
4	R=OCOC$_6$H$_4$NO$_2$	90	[41]
5		90	[44]
6	*trans* *cis*	80	[44]
7		20	[48]
8		25	[48]
		15	[48]
9	R=CH$_3$	50	[45]
10	R=CF$_3$	34	[45]
11	$(CH_3)_2CF(CH_2)_3CO_2CH_2CCl_3$	55	[47]
12	$(CH_3)_2CFCH_2CO_2CH_2CCl_3$	30	[47]
13	$CH_3CFCH_2CO_2CH_3$ $CH_2CO_2CH_3$	2	[47]

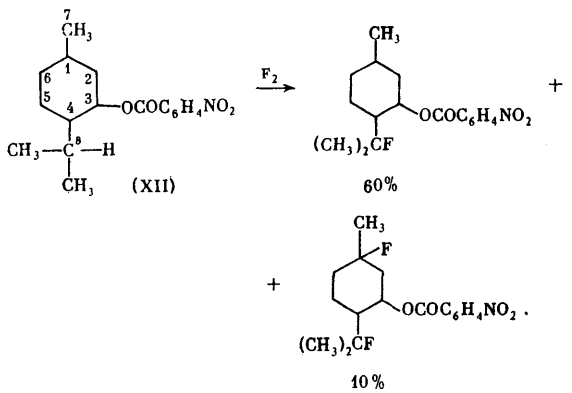
[a] Depending on the reactivity of starting material from 1 to 100 moles fluorine were passed in per mole substrate.
[b] Starting materials differed in that hydrogen replaces fluorine.
[c] Yield calculated on substrate.

1-Fluorobicyclo[2.2.2]octane and 2-fluorobicyclo[3.2.1]octane (rearrangement product) were obtained from the reaction. The authors proposed a scheme explaining the formation of these products. In the first stage a pentacoordinated carbonium ion (IX) is formed which is in equilibrium with the non-classical ion (X) having 8 electrons at each carbon atom. However such an explanation is hardly acceptable since conversion of ion (IX) to any other carbonium ion may only be effected by direct elimination of proton with subsequent protolysis of other σ bonds. Just such a scheme has been proposed for the isomerisation of saturated hydrocarbons in strongly acidic medium.[50] It is probable that the rearrangement product may be formed only from ion (XI) which has a strong electron-accepting substituent (fluorine atom) in the β-position and consequently must be less stable than ion (IX).

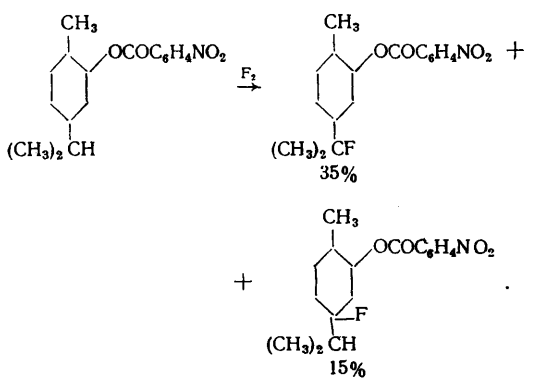


(XI)

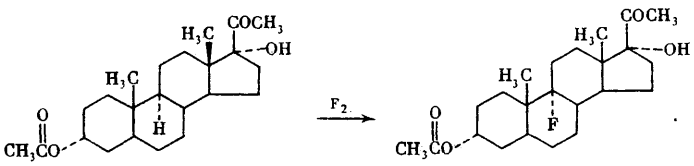
A relationship was found between the contribution of the *p*-orbitals to the C–H bond and the ease of replacement of the hydrogen atom; the greater the contribution of *p*-orbitals then the easier substitution occurred.[46] According to semi-empirical calculations by the PRDDO method the contribution of *p*-orbitals to the C(1)–H bond is 2.7 and C(4)–H and C(8)–H about 2.9. The product with substitution at C(8) was obtained preferentially.



The fact that substitution did not occur at C(4) was explained by the authors by the fact that fluorine approaches the reaction centre accompanied by at least one molecule of chloroform and the C(4) atom is the most sterically hindered. If the ester substituent is removed then the hydrogen atom at C(4) is also replaced.



However in our opinion it is more certain that this fact is explained by the deactivating influence of the electron-accepting ester group on the vicinal hydrogen atom of compound (XII). The synthesis of fluorosteroids is the most useful preparative application of the selective replacement of hydrogen atoms with elementary fluorine.[38] It was recorded that in all cases replacement occurred with retention of configuration. As a rule yields of products were not large (20–30%) but for 5α-pregnane-3α,17α-diol-20-one 3-acetate (XIII) the yield of 9α-fluorosteroid (XIV) reached 60%.



(XIII) (XIV)

The selectivity of the replacement attracts attention. Of the three tertiary hydrogen atoms in compound (XIII) only the 9α-hydrogen, which is furthest from the electron-accepting substituents, is replaced by fluorine.

The fact that fluorination takes place with complete retention of configuration and also the absence of typical carbocation rearrangements (excluding bicyclo[2.2.2]octane) and the absence of proton elimination reactions indicated, in the authors' opinion,[46] against a hydride transfer mechanism:

$$R_3CH + F_2 \rightarrow R_3C^+ + HF \xrightarrow{F^-} R_3CF.$$

They ascribed the selective fluorination to a type of electrophilic substitution at the saturated carbon atom proceeding through a pentacoordinated carbonium ion (XV) (Olah mechanism):

$$R_3CH + F_2 \rightarrow \left[R_3C\text{-}\overset{H}{\overset{\diagup}{\underset{F}{\diagdown}}}\ F^- \text{---} HCCl_3\right] \xrightarrow{-HF} R_3CF.$$

In this reaction chloroform is a trapping agent for free radicals and a source of protons and serves as an acceptor of fluoride anion through a hydrogen bond which lowers the energy of the transition state.

It has recently been shown that not only elementary fluorine but also halogen fluorides may be used for the selective replacement of hydrogen atoms by fluorine.[51–53] Both tertiary and secondary hydrogen atoms are replaced by this method. Chlorine trifluoride in an inert solvent (Freon 114, 112, liquid CO_2) at −75 °C fluorinates hydrocarbons in good yield on observing experimental conditions such that ClF_3 itself and inorganic byproducts are in the reaction zone for no more than 2 min.[51] Reaction proceeds according to the scheme:

$$-\overset{|}{\underset{|}{C}}-H + ClF_3 \rightarrow -\overset{|}{\underset{|}{C}}-F + HF + ClF.$$

The formation of chlorine monofluoride as an inorganic byproduct was established by trapping it with cyclohexane or ethylene. Under these conditions first tertiary and then secondary hydrogen atoms are preferentially replaced. Methane and 2,2,3,3-tetramethylbutane, having only primary hydrogen atoms do not react. Since in the case of 2,2-dimethylbutane and 2-methylbutane products are obtained with 1,2-migration of methyl groups the authors preferred a heterolytic mechanism for the replacement of hydrogen by fluorine:

$$(CH_3)_3CCH_2CH_3 + ClF_3 \rightarrow ClF + HF + F^- + (CH_3)_3C^+CHCH_3 \rightarrow$$
$$\rightarrow (CH_3)_2C^+CH(CH_3)_2 \xrightarrow{F^-}$$
$$\rightarrow \underset{55\%}{(CH_3)_2CFCH(CH_3)_2} \xrightarrow{ClF_3} \underset{22\%}{(CH_3)_2CFCF(CH_3)_2},$$
$$(CH_3)_2CHCH_2CH_3 \xrightarrow{ClF_3} \underset{33\%}{(CH_3)_2CFCH_2CH_3} \xrightarrow{ClF_3}$$
$$\rightarrow \underset{5\%}{CH_3CF_2CH(CH_3)_2}.$$

Bromine trifluoride in a Freon medium at room temperature is also capable of replacing a hydrogen atom by fluorine. Reaction was carried out by direct addition of liquid BrF_3 to a 5–20% solution of substrate in Freon.[52,53] The process occurs according to the scheme:

$$R_3CH + {}^2/_3BrF_3 \rightarrow R_3CF + HF + {}^1/_3Br_2.$$

Selective fluorination of esters containing tertiary hydrogen atoms was effected by such a method.

$$(CH_3)_2CHCH_2OCOCF_3 + BrF_3 \rightarrow \underset{47\%}{(CH_3)_2CFCH_2OCOCF_3}.$$

Bromine trifluoride in the presence of anhydrous hydrogen fluoride (60 mol%) is capable of replacing tertiary hydrogen atoms in the position α to an ester group, which was unsuccessful with elementary fluorine.

$$(CH_3)_2CHCO_2R_F + BrF_3 \xrightarrow[\text{Freon 113}]{HF} \underset{50\%}{(CH_3)_2CFCO_2R_F} +$$
$$+ \underset{8\%}{CH_2BrCFCO_2R_F},$$
$$\quad\ \ CH_3$$

$$R_F = CH_2(CF_2)_2H.$$

On replacing hydrogen atoms with bromine trifluoride the formation of cationoid moieties at the stage determining the reaction products was confirmed by the observation of a methyl group 1,2-migration in the reaction with 2-fluoro-2-methylbutane:[53]

$$(CH_3)_2CFCH_2CH_3 + BrF_3 \rightarrow$$
$$\rightarrow \underset{85\%}{CH_3CF_2CH(CH_3)_2} + \underset{15\%}{(CH_3)_2CFCHFCH_3}.$$

On extended reaction of bromine trifluoride with polyhaloalkanes in a Freon medium nonselective replacement of hydrogen atoms by fluorine was observed:[54]

$$CH_2FCHFCH_2Cl \xrightarrow[\text{Freon 112}]{BrF_3} \underset{29\%}{CH_2FCHFCH_2F} + \underset{35\%}{CHF_2CHFCH_2Cl} +$$
$$+ \underset{6\%}{CH_2FCF_2CH_2Cl} + \underset{29\%}{CHF_2CHFCH_2F}.$$

It should be mentioned that replacement of chlorine atoms in haloalkanes under the action of BrF_3 is catalysed by $SnCl_4$ and $SbCl_5$ (Lewis acids forming complex salts with BrF_3) while replacement of hydrogen atoms is catalysed by anhydrous HF.[55]

$$CH_2ClCHFCH_2Cl \begin{cases} \xrightarrow[SnCl_4(1\%)]{BrF_3} \underset{28\%}{CH_2ClCF_2CH_3} + \underset{43\%}{CH_2ClCHFCH_2F}, \\ \xrightarrow[HF]{BrF_3} \underset{30\%}{CH_2ClCF_2CH_3} + \underset{15\%}{CH_2ClCHFCH_2F} + \underset{25\%}{CHF_2CHFCH_2Cl}. \end{cases}$$

On fluorinating 1,3-dichloro-2-fluoropropane in Freon 113 in the presence of $SnCl_4$ only products of chlorine replacement were obtained while in HF 3-chloro-1,1,2-trifluoropropane, the product of replacing a hydrogen atom, was also obtained.

It has been shown[1] that in oxidative replacement of halogen atoms in organic halo-derivatives, halogen fluorosulphates are closest in reactivity to halogen fluorides. Consequently it might be expected that these reagents will also efficiently oxidise ether C–H bonds. However a single example of oxidative replacement of a hydrogen atom under the action of bromine trisfluorosulphate has been described in the literature.[56]

$$Cl(CF_2)_4H + Br(OSO_2F)_3 \rightarrow Cl(CF_2)_4OSO_2F + BrOSO_2F + HSO_3F.$$
65%

It is difficult to agree with a study[57] which considered that halogen fluorosulphates are inert towards C–H bonds at room temperature and only replace halogen atoms. In the case in question the matter consists not in the inertness of halogen fluorosulphate towards C–H bonds but in the fact that iodine and bromine atoms in alkyl halides are oxidised significantly more slowly than hydrogen atoms. The absence of data on reactions of halogen fluorosulphates with saturated hydrocarbons is also seemingly linked with the extremely low stability of alkyl fluorosulphates which complicates the isolation of the primary substitution products.

V. Reactions of saturated organic compounds with ozone

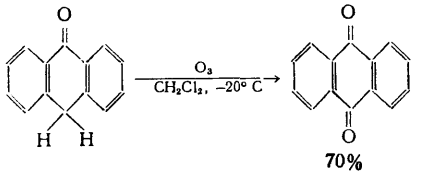
Linked with the current ecological concern about the opacity of the Earth's ozone layer, significant attention has been paid to the reaction of ozone with saturated hydrocarbons[58–70] and at the present time this is the most studied class of reactions for the oxidative replacement of hydrogen atoms. The reaction of ozone with σ C–H bonds leads to the formation of hydrotrioxides (XVI) as initial products which at temperatures greater than −40 °C readily decompose with the formation of alcohols and carbonyl compounds.

$$R_2CH_2 + O_3 \rightarrow \underset{(XVI)}{R_2CH_2OOOH} \rightarrow [R_2CHO^{\cdot} + {}^{\cdot}OOH]$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

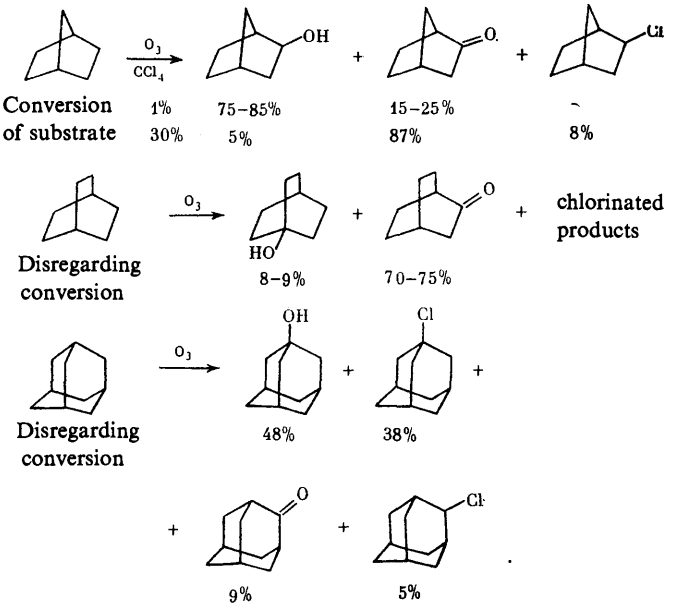
$$R_2CHOH + O_2 \qquad R_2C{=}O + H_2O_2 \qquad RCHO + R^{\cdot}.$$

$R_2CH\dot{O}$ and $\dot{O}_2H$ radicals escaping from the cage initiate radical processes. Usually ozonation of saturated hydrocarbons is effected by passing ozone diluted with nitrogen or oxygen into a solution of substrate in an inert solvent (CCl_4, CH_2Cl_2, Freons) at a temperature between −78 and +25 °C. Ozonation of anthrone carried out by this method leads to the formation of anthraquinone in 70% yield.[58]



70%

The authors showed that 2 moles O_3 were consumed and 2 moles O_2 were liberated on oxidising 1 mole anthrone confirming the sequential replacement of two atoms of hydrogen. An investigation of the oxidation products of norbornane, bicyclo[2.2.2]octane and adamantane has been described.[59] Both the tertiary hydrogen atoms at the bridge-head and the secondary hydrogen atoms were replaced in adamantane and bicyclo[2.2.2]octane but only secondary atoms in norbornane.



An interesting method of hydroxylation of tertiary C–H bonds has been developed.[60] Ozonation was carried out by absorbing substrate (1%) on silica gel and passing a stream of ozone (3% in O_2) at −45 °C. Rupture of C–C bonds was observed in addition to replacement of hydrogen atoms. Thus interaction of 2,3-dimethylbutane with O_3 led to the following set of products:

$$(CH_3)_2CHCH(CH_3)_2 \xrightarrow{O_3}$$

$$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}H(CH_3)_2 + (CH_3)_2\underset{\displaystyle O}{\underset{\|}{C}}HCCH_3 + (CH_3)_2CO.$$

35% 28% 37%

The total yield of ozonation products was 80–90%. The authors noted that on ozonation in Freon 112 solution at −45 °C the conversion of substrate was significantly less but the composition of products was the same as on silica gel. Thus on ozonation of 3-methylpentane the yield of products was only 6%.

Hydrotrioxides stable at low temperatures were obtained on ozonation of acetals with ozone and were characterised by their NMR spectra.[61] The hydrotrioxides decomposed by a radical mechanism to oxygen and the corresponding hydroxy derivatives, which gave esters and alcohols on acidic catalysis:

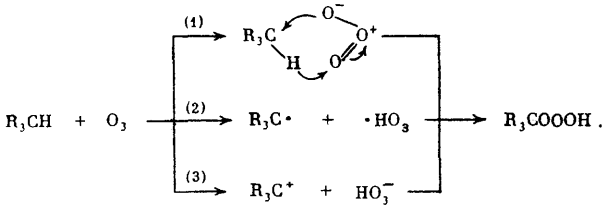
$$CH_3\underset{\displaystyle H}{\underset{|}{C}}(OR)_2 \xrightarrow{O_2} CH_3\underset{\displaystyle O_3H}{\underset{|}{C}}(OR)_2 \rightarrow$$

$$\rightarrow O_2 + CH_3\underset{\displaystyle OH}{\underset{|}{C}}(OR)_2 \xrightarrow{H^+} CH_3CO_2R + ROH.$$

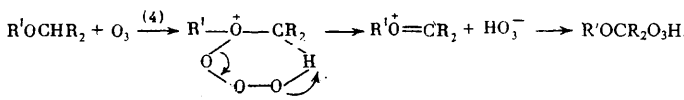
Replacement of hydrogen atoms at a saturated carbon atom by ozone occurs pre-eminently with retention of configuration. Thus on ozonation of *cis*- and *trans*-1,4-dimethylcyclohexanes 80–90% retention of configuration was observed,[62] oxidation of *cis*- and

trans-decalins to the corresponding 9-decalols occurred with complete retention of configuration.[63]

Many studies have been devoted to the kinetics and mechanism of ozonation of C–H bonds.[59,64–70] Three possible mechanisms have been proposed for the first stage of the oxidation of saturated hydrocarbons with ozone:



A mechanism with initial attack of ozone at the oxygen atom is possible for ethers and acetals in addition to those indicated above:



However it was shown that on oxidation of t-butylbenzyl ether[64] and also of a series of hydrocarbons[65,66] the kinetic isotope effect was approximately 4. These data make it possible to consider scheme (4) unlikely.

An assessment has been carried out of the possible routes of the ozonation reaction of saturated hydrocarbons by empirical calculation methods in the application of transition state theory based on recent thermochemical data.[62] It was shown that the most probable mechanism involved transfer of hydride ion and the formation of a tight ion pair:

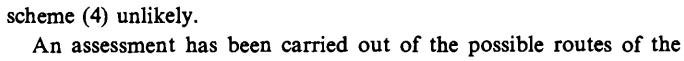


Table 3. Relative rates of ozonation,[67,68] bromination[71] and solvolysis.[72]

Type of C–H bond	O_3	Br·	Solvolysis[a]
Primary	0.003	0.005	—
Secondary	1	1	1
Tertiary	100	88	$10^{7.8}$

[a] Solvolysis rate in 80% alcohol of 2-bromoadamantane and 2-bromo-2-methyladamantane.

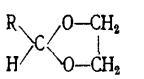
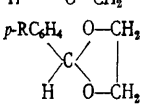
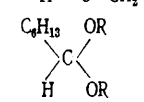
However study of the kinetics of oxidation of saturated hydrocarbons place the hydride ion transfer mechanism in doubt.

Relative rates of ozonation of primary, secondary and tertiary C–H bonds are shown in Table 3 as are relative rates of the free radical bromination and solvolysis.

The observed ratios of ozonation rates showed that a significant positive charge is not generated on the α-carbon atom in the transition state as in that case the difference in reactivity would be significantly greater. Since nucleophilic assistance by the solvent is absent from solvolysis of adamantane derivatives the ratio shown in Table 3 reflects the stability of transition states close in structure to a carbocation. It should be mentioned that ozonation is closer to free radical bromination in selectivity (a polar transition state is characteristic of the latter) than to a carbocationic reaction.

A kinetic study of oxidation processes with a change of substituent for various systems showed that the logarithm of the relative rate constants correlated well with the Hammett and Taft constants (Table 4).

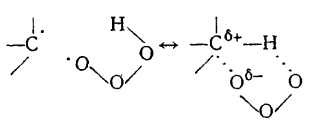
Table 4. Correlation of kinetic data and Hammett and Taft constants.[69,70]

No.	Substrate	ρ
1		−1.16
2		−1.10
3		−1.31
4	p-$RC_6H_4CH_3$	−2.07
5	p-$RC_6H_4CH_3$[a]	−1.42

[a] Reaction parameter for free radical bromination.[71]

The small values of ρ obtained for acetals were explained either by the fact that the positive charge in the transition state is stabilised by the acetal oxygens and to a significantly lesser degree by the substituents or by the fact that a small positive charge is generated in the transition state. For comparison values of ρ in acid hydrolysis reactions of acetals were from −3.6 to −4.2.[73] Comparison of ozonation and free radical bromination shows (Table 4, Nos. 4, 5) that oxidation with ozone proceeds through a more polar transition state than does bromination. The effect of solvent polarity on the ozonation rate of C–H bonds has been investigated.[68,69] It was shown that the oxidation rate of 2-hexyl-1,3-dioxan with ozone in acetic anhydride was two times greater than in n-hexane.[69] A similar increase in rate of 2–2.5 times on going from carbon tetrachloride (ε = 2.24) to acetonitrile (ε = 38) was observed on oxidation of a series of ethers. For comparison the solvolysis rate of t-butyl iodide was increased by more than one order of magnitude on going from benzene (ε = 2.28 to benzonitrile (ε = 25).[71] Thus the available data permit the view that the ozonation of C–H bonds proceeds through fairly polar transition states, however the charge separation in the transition state does not reach values characteristic of carbocationic reactions.

Activation parameters have been determined for the ozonation of a series of saturated hydrocarbons, ethers and acetals.[68,69] The energy of activation of these reactions is between the limits of 5 to 15 kcal/mol, the pre-exponential multiplier varies from 6 to 8. The values obtained for the pre-exponential factor are somewhat greater than would be expected for an insertion mechanism (log A < 7) [74] and less than for the usual radical reactions (log A = 8−11).[71] However the fact that ozonation proceeds through a more polar transition state than free radical substitution should be taken into consideration and this must lead, especially on carrying out the reactions in non-polar solvents, to an increase in the negative entropy of activation. Further the pre-eminent retention of configuration characteristic of ozonation may be explained not only by the insertion mechanism but also by the rapid collapse of the free radical pair in the solvent cage. Such an explanation of the pre-eminent retention of configuration was proposed[75] for the oxidation of saturated hydrocarbons by chromic acid to the corresponding alcohols. The mechanism of direct insertion of oxidising agent at a C−H bond is unlikely since it was shown that the sterically more hindered triethylmethane is oxidised 1.5 times more rapidly than isobutane. Thus the transition state in the ozonation reaction is most probably described by two resonance structures.

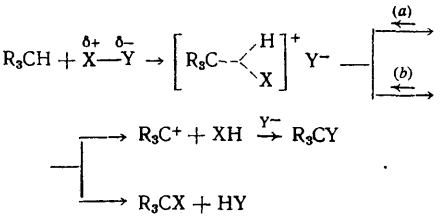


VI. General rules and mechanisms for oxidative replacement of hydrogen in saturated hydrocarbons

The experimental data considered in the previous sections show that in practice all strong oxidising agents, viz. elementary fluorine, ozone, nitronium salts or halogen fluorides are capable at low temperature in the liquid phase of selectively attacking a σ-C−H bond leading to the replacement of hydrogen by another element or functional group. The following factors are capable of increasing the selectivity of the oxidative replacement of hydrogen: 1) there must not be many C−H bonds in the substrate molecule of identical reactivity and 2) the more reactive the substrate the greater the dilution by inert solvent of substrate and reagent is required to bring about a selective reaction. An increase in electron density of the C−H bond favours attack by oxidising agent since the following series of C−H bond reactivities was observed for all the reactions considered in the previous sections: tertiary > secondary ≫ primary. Correspondingly the introduction of electron-accepting substituents into the substrate molecule deactivates the neighbouring C−H bond and in this way the selectivity of replacing more distant hydrogen atoms is increased.

In the general case the non-radical reaction pathway of replacing hydrogen atoms under the action of oxidising reagents may be described by the scheme proposed by G Olah (Scheme 1).[50] Simple C−H bonds possess the ability to give a bonded electron pair to an electrophilic reagent with the formation of two-electron three-centre bonds. The electrophile attacks covalent bonds just from the front not the rear, and those portions of the covalent bond orbitals play a relatively small role. Subsequent breakdown of the three-centre bond in the pentacoordinate carbonium ion (XVII) may lead either to the formation of trivalent carbenium ions (route *a*) or directly to bonding carbon with the electrophile and ejection of a proton (route *b*).

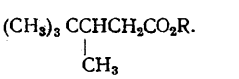
Scheme 1



Replacement of hydrogen atoms by scheme 1*a* should be referred to as a nucleophilic substitution reaction and by scheme 1*b* as a direct electrophilic replacement at a saturated carbon atom. At the present time it appears extremely difficult to choose between these directions for the majority of oxidative replacements of hydrogen. Thus in the case of homoatomic oxidising agents (F_2, O_2, Hal_2−Lewis acids) it is impossible to make this choice on the basis of the nature of the products since in both cases the same products will be formed. Consequently the scheme of direct electrophilic replacement quoted for these reactions in the fundamental publication[76] does not have adequate foundation.

The authors present a series of arguments in favour of electrophilic substitution as the course of the reaction of elementary fluorine with hydrocarbons, however in our view it is impossible to regard the mechanism of this reaction to be unequivocally established.

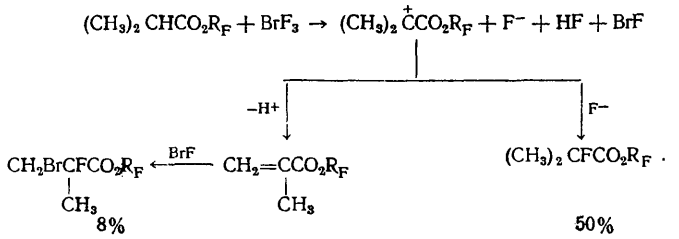
The first argument is the absence of rearrangements characteristic of carbenium ions. This principle, discovered by the authors, is not unexpected since only tertiary hydrogen atoms were subjected to substitution and rearrangements are not characteristic for tertiary carbocations. It would be extremely interesting to investigate fluorination of substrates for which rearrangements are possible, for example:



The second argument is the absence of elimination reactions. Proceeding from the general reaction rules of carbenium ions obtained from study of solvolysis reactions it would certainly be expected that unsaturated compounds would be formed on carrying out a fluorination reaction through a carbenium ion, especially in a non-polar solvent. However under these conditions the resulting olefins will be subjected to further fluorination and consequently small quantities of difluoro adducts will be difficult to detect among products of radical fluorination.

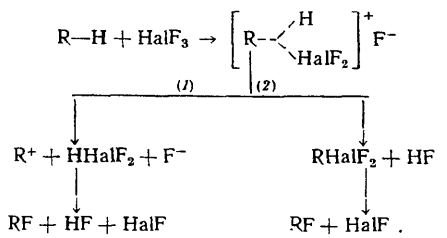
Further it should be mentioned that the formation of olefins is not a characteristic of hydrogen replacement reactions under the action of ClF_3 and BrF_3, although tertiary carbocations are formed in these reactions. Probably this is linked with the small steric volume of the nucleophile (fluorine anion) and also with conducting these reactions at low temperatures. Nonetheless in the reaction of fluoroalkyl isobutyrate with BrF_3 in addition to the main product, fluoroalkyl 2-fluoroisobutyrate, a small quantity of fluoroalkyl 2-fluoro-3-bromoisobutyrate was isolated[52] which was

probably formed as a result of bromofluorination of the unsaturated ester:



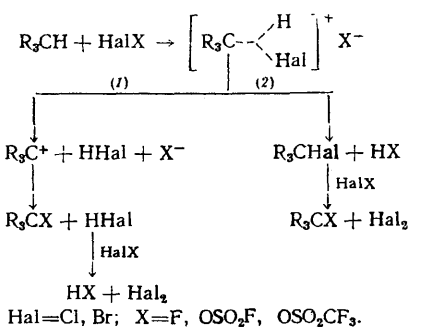
The main argument in favour of electrophilic substitution is the formation of products with complete retention of configuration from optically active substrates. However these results were obtained for conformationally stable cyclohexane derivatives, there are no data on the stereochemistry of oxidative substitution of hydrogen atoms in aliphatic compounds. It is known that the replacement reaction may proceed with the formation of carbenium ions and is accompanied by retention of configuration in the case when the reaction proceeds in a tight ion pair.[71]

In hydrogen replacement reactions with halogen fluorides (ClF_3, BrF_3) the formation of carbocationic intermediates at the stage determining the reaction products has been unambiguously confirmed by the observation of 1,2-migration of methyl groups. However two reaction routes may be proposed in this case:



Conversion of alkylhalogen(III) difluoride into final product may be accompanied by rearrangements. Thus dissociation of neopentyliodine(III) difluoride occurs with methyl group migration and the formation of t-amyl chloride and trimethylethylene derivatives.[1]

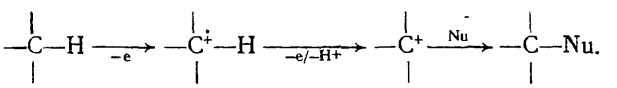
On the whole, for any oxidising agent containing an electropositive halogen atom, it is impossible to draw a conclusion as to the direction (route *1* or *2*) of the reaction based on the reaction products. At present it is well known that such oxidising agents preferentially attack the unshared electron pairs of halogen atoms covalently bonded to carbon rather than a C—H bond in identical surroundings.[1] Consequently if the reaction also proceeds according to route *2* then the product obtained R_3CHal will be slowly converted into product R_3CX undergoing in this route all the rearrangements and migrations typical of this reaction.



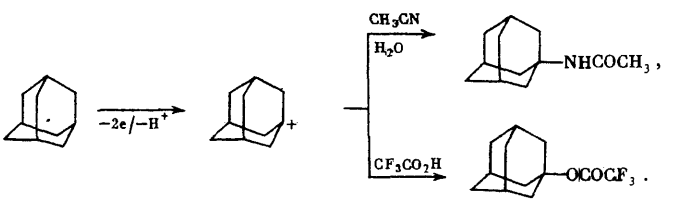
Therefore irrespective of the reaction route the final products of the interaction of hydrocarbons with halogen-containing oxidising agents will be the same.

It might have seemed that reasoned conclusions on the possible routes of hydrogen replacement by scheme 1 may be drawn on the basis of results of nitronium salt oxidation of hydrocarbons. In a non-nucleophilic medium (CH_2Cl_2, sulpholan) nitro derivatives are obtained in low yield the formation of which may be explained by electrophilic substitution (route *b*). The formation of 1-nitroadamantane shows that attack at a C—H bond is effected from the front since attack from the rear is impossible for adamantane. However on carrying out these reactions in nucleophilic solvents (CH_3CN, CF_3CO_2H) the corresponding acetamides and trifluoroacetates were formed in high yield which, together with the observed sextet rearrangements and elimination reactions, points in favour of splitting off a hydride ion with the formation of carbenium ion (route *a*).

The great similarity between the results of the hydrogen replacement reactions under the action of oxidising agents and the results of electrochemical oxidation of similar compounds has attracted attention.[34,77–79] In the light of modern ideas the formation of a carbenium ion in electrochemical oxidation of saturated hydrocarbons occurs as a result of two sequential one-electron oxidations, which is formally equivalent overall to hydride ion elimination by the reagent, i.e. the oxidising agent:[34]



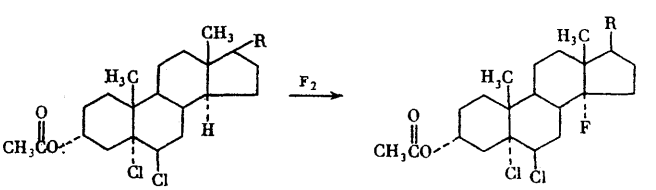
Depending on the solvent and electrolyte used, corresponding functional derivatives are formed, for example:



Yields of trifluoroacetates and acetamides were 50—90%.[69,77] As indicated previously similar results were obtained with nitronium salts.

It should be added that if terminology is applied strictly then the proposed elimination of hydrogen by an electron pair under the action of an oxidising agent cannot be called hydride ion elimination since the attacking electrophilic particle (E) possesses more strongly electron-accepting properties than hydrogen and a molecule with an electropositive hydrogen atom is the leaving group.

A particular special feature may be noted for certain oxidising agents containing electropositive oxygen or fluorine atoms, viz. their greater affinity towards hydrogen than towards chlorine (in the same environment). Such data are rare at present but they merit attention.



Oxidising agents with an electropositive halogen oxidise chlorine atoms under identical conditions.[1]

$$CH_3(CH_2)_5Cl + BrF_3 \rightarrow CH_3(CH_2)_3CHFCH_3.$$

The oxidising replacement reactions for hydrogen considered have one further special feature concerning their preparative use. Although tertiary and secondary C–H bonds are readily oxidised some final substitution products are unstable under the usual conditions in the case of simple hydrocarbon substrates. Thus secondary and tertiary fluorides, fluorosulphates and related compounds are readily decomposed especially in the presence of traces of strong acid. However introduction of electron-accepting substituents into a substrate increases the stability of such compounds and under these conditions interesting preparative applications may be considered for the oxidative hydrogen replacements.

Summarising the results considered the following conclusions may be drawn:

1. At the present time there are no conclusive data confirming the possibility of electrophilic substitution of hydrogen at an sp^3-hybrid carbon under the action of oxidising agents.

2. Carbenium ions are formed at the stage determining the products of oxidative replacement of hydrogen.

Further investigations are necessary for a deeper understanding of the mechanism of the above reactions. In particular it is necessary to expand ideas on the oxidation of C–H bonds at sp^3-hybrid carbon atoms by reagents such as halogen fluorides, hypohalites of strong acids and nitronium salts.

In conclusion it would be desirable to record that at present chemists have available a large selection of oxidising reagents for the selective functionalisation of saturated hydrocarbons and it may be expected that in the next few years the preparative potential of these reactions will be appreciably expanded.

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Reactions of pyridines, pyrimidines and 1,3,5-triazines with nucleophilic reagents

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ABSTRACT. Literature data published since 1971 on the addition of nucleophiles to the C=N bond of the most studied π-deficient six-membered heterocycles, viz. pyridine, pyrimidine and 1,3,5-triazine leading to their transformation have been examined and correlated. Possible applications and proposed mechanisms for the considered processes have been discussed.

The bibliography contains 169 references.

CONTENTS

I. Introduction 514
II. Recyclisation of pyridines, pyrimidines and 1,3,5-triazines under the action of water, alkali, amines, and strong acids 514
III. The Dimroth and Kost–Sagitullin reactions 518
IV. Recyclisations during hydrazinolysis 520
V. Reactions with alkali metal amides in liquid ammonia 521
VI. Conversions with CH-acids and ambident nucleophiles 523

I. Introduction

Nitrogen atoms of the pyridine type in six-membered nitrogen-containing aromatic compounds redistribute the electron density such that the carbon atoms in the heterocycle are depleted of electrons.[1,2] The maximum deficiency of negative charge is formed in the positions *ortho* and *para* to the hetero atom.[2] The angle between the valence bonds of nitrogen and carbon in heterocycles of such type differ from 120°.[3] The above mentioned reasons facilitate the addition of nucleophilic reagents at the C=N bonds of these rings. Among the considered compounds the uncondensed azines lie in the series 1,3,5-triazine > pyrimidine > pyridine in reactivity towards nucleophiles in accordance with the decrease in π-deficiency.[1]

In several cases the addition of nucleophiles to these heterocycles leads to transformations of the latter.

Conversions of heterocycles known up to 1971 have been collated in a review.[4] Separate problems on recyclisation under the action of certain nucleophilic reagents have been considered in reviews for pyridines,[7,13] pyrimidines[5,6,10,12] and other azines.[8,9,11]

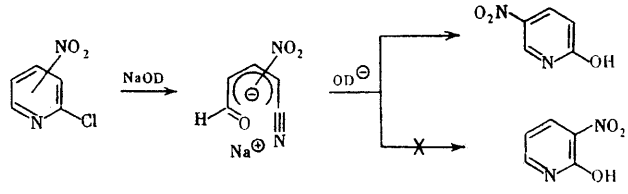
A large number of studies has been published in the chemical literature in the last decade on such transformations the analysis and correlation of which for uncondensed pyridines, pyrimidines and 1,3,5-triazines is the subject of the present review.

II. Recyclisation of pyridines, pyrimidines and 1,3,5-triazines under the action of water, alkali, amines, and strong acids

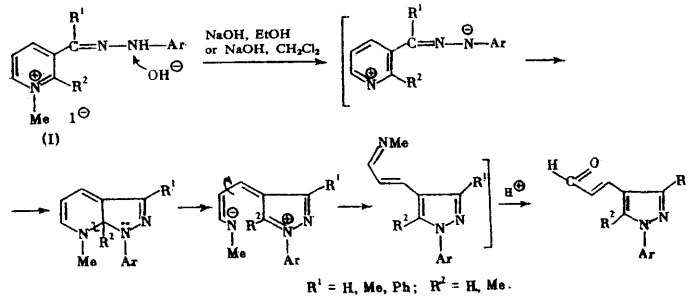
Pyridines, having only one nitrogen atom, are the most 'aromatic' among the compared heterocycles and are least inclined to interact with nucleophiles. In order to facilitate addition of nucleophilic reagents at the C=N bond of the pyridine ring their quaternary salts are usually used.[3,7,13] An analogous method is frequently applied in the case of pyrimidine compounds characterising high reactivity towards nucleophiles. The three nitrogen atoms of 1,3,5-triazines show such high overall electron-accepting action that these molecules are sufficiently activated for reaction with nucleophiles without quaternisation.

The products of cleaving pyridinium salts by nucleophiles are derivatives of glutaconic aldehyde which are used in organic synthesis for cyclisation into derivatives of pyridine and other heterocycles.[13]

Derivatives of glutaconic aldehyde are formed on heating 2-chloropyridines having a nitro group in the 3 or 5 positions with alkali. However these cyclise once more into a pyridine compound but only a 5-nitropyridine derivative.[14]

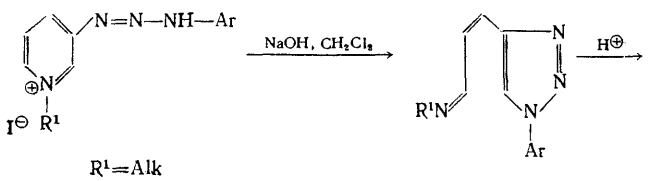


3-Arylhydrazonomethyl-1-methylpyridinium iodides (I) are converted into acroleylpyrazoles in the presence of base. According to the proposed mechanism, under the action of base a negative charge arises on the nitrogen atom of the hydrazone fragment in (I) and this aids intramolecular cyclisation. Rupture of the pyridine ring then occurs and a pyrazole derivative is formed.[15,16]

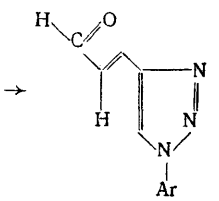


As might have been expected from the conversion scheme electron-donating substituents R^1 in (I) reduce the yield of pyrazole derivative. A substituent R^2 in (I) also shows a negative effect on the course of the reaction due to steric hindrance when forming the intermediate bicyclic compound.

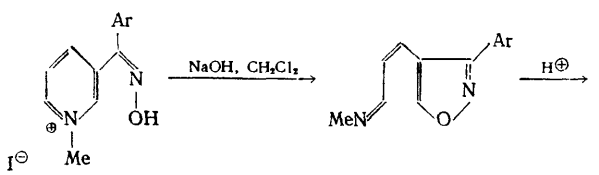
If the $R^1-C=$ fragment in the pyridine salt (I) is replaced by nitrogen then the 3-(3′-aryl-1′-triazenyl)-1-methylpyridinium salt is converted under the above conditions by an analogous scheme into a 1,2,3-triazole derivative.[16,17]

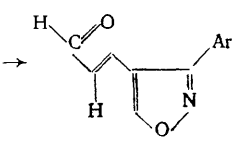


R^1=Alk

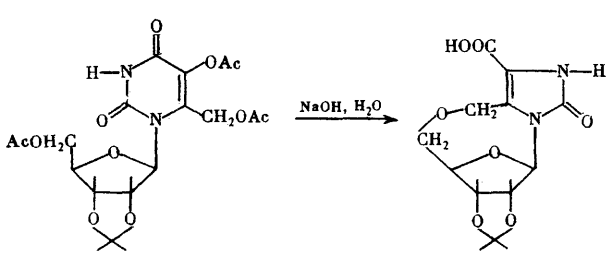


Derivatives of isoxazole are formed by a similar reaction from oximes of 3-benzoyl-1-methylpyridinium iodides in 10% yield.[16,17]





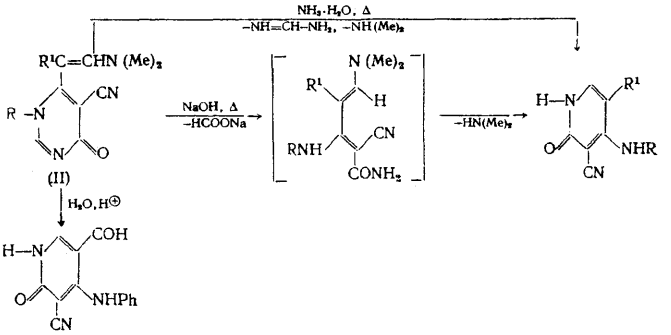
Uracil compounds are converted by alkali into imidazolones which are used in nucleic acid chemistry.[18]



Similar conversions of the pyrimidine nucleus into imidazolones occur in aqueous solutions of amines or alkali and also in the case of pyrimido[4,5*e*]1,2,4-triazines.[19,20]

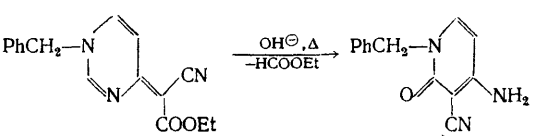
1,6-Disubstituted 5-cyano-4-oxo-1,4-dihydropyrimidines (II) are decomposed on boiling in dilute alkali with fission of the C(2)–N(1) and C(2)–N(3) bonds with separation of formic acid salts. Cyclisation of the resulting intermediate occurs through the dimethylaminovinyl fragment with cleavage of dimethylamine.[21–24] A similar conversion of (II) (R = $PhCH_2$, R^1 = H) occurs on boiling with aqueous ammonia with cleavage of formamidine.[25]

In the case of hydrolysis of (II) (R = Ph, R^1 = H) with acid the recyclisation product was 3-cyano-5-formyl-2-oxo-4-phenylamino-1,2-dihydropyridine.[26]

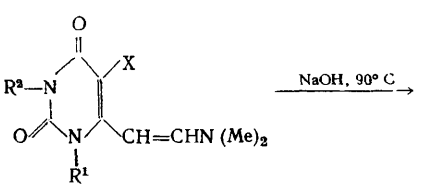


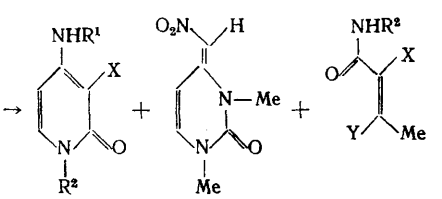
R^1, R = $-(CH_2)_n-$, n = 2,3; R = $PhCH_2$, Ar, cyclohexyl, R^1 = H.

Alkaline hydrolysis of 1-benzyl-4-(ethoxycarbonylcyanomethylene)-1,4-dihydropyrimidine also led to a 2-pyridone derivative.[27]



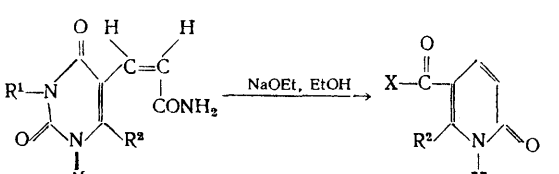
6-Dimethylaminovinylated derivatives of uracil are converted on heating in alkali into 2-pyridone derivatives with the formation of pyrimidines and acyclic compounds as side products.[28,29]





X=NO_2, CN; Y=R^1NH, OH;
R^1=Me, Ph, $PhCH_2$; R^2=Me, $C_6H_{11}Ar$

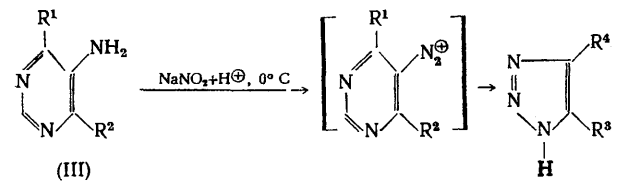
5-(2′-Carbamoylvinyl)uracils with sodium ethoxide in ethanol form 5-carbamoylpyrid-2-ones the ratio of which depends on the amount of water added to the reaction mixture.[30]



R^1R^2=H, Alk; X=R^1NH, OEt.

Unsubstituted pyrimidine is converted into 5-ethyl-2-methylpyridine on heating with aqueous methylamine in a sealed tube.[31]

4,6-Disubstituted 5-aminopyrimidines containing no labile hydrogen atoms in the 4 and 6 positions form 4,5-disubstituted 1,2,3-triazoles on treatment with nitrous acid.[32–35]

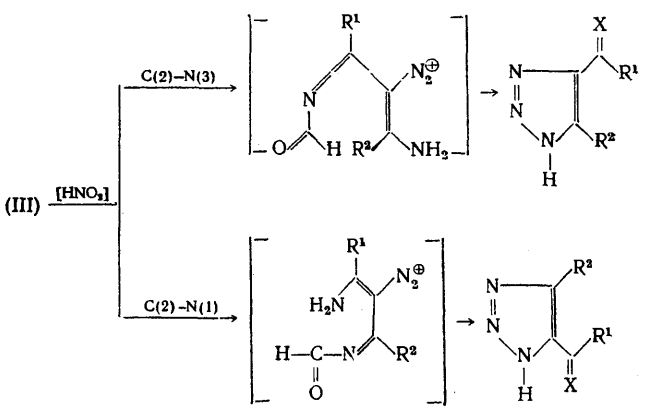


(III)

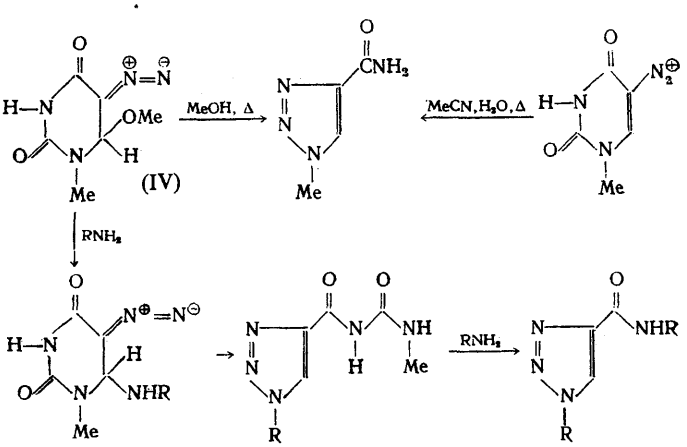
R^1=OMe, $N(Me)_2$, OEt; R^2=SAlk, SAr, SHetar, $N(Me)_2$, Cl, OMe, OEt; R^3=R^2, CN, $C(=Y)R^2$, where Y=NH, O;

R^4=COOMe, COOEt, CN, $C(=O)SR$.

It is presumed that diazonium salts are formed initially which are subjected to covalent hydration at position 2 of the pyrimidine ring. The presence of a methyl group in the second position of (III) had no effect on the course of hydration. Then either the C(2)–N(1) or the C(2)–N(3) bond in the pyrimidine ring may break. The obtained intermediates are cyclised into 1,2,3-triazole derivatives.[32–35]



Diazonium salts of the uracil series are converted on heating in methanol or aqueous acetonitrile by fission of the N(1)–C(2) bond of the pyrimidine nucleus into 4-carbamoyl-1-methyl-1,2,3-triazole.[36,37]

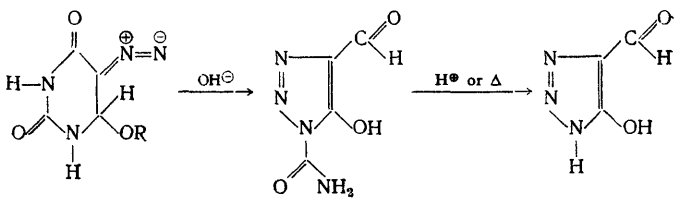


(IV)

R=Alk, $-CH_2CH=CH_2$, $-(CH_2)_3N(Me)_2$.

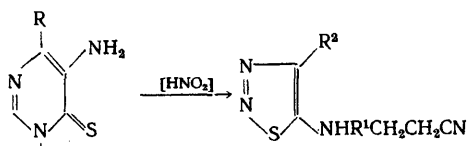
Compound (IV) forms 1,2,3-triazoles by reaction with various primary amines.[38,39] Possibly primary amines initially replace the alkoxy residue of (IV) and then fission of the C(6)–N(1) bond occurs with closing of the five-membered 1,2,3-triazole ring and inclusion in it of the amino group nitrogen. Similar reactions take place for 3-methyl and 1-desmethyl derivatives of (IV).

Alkaline hydrolysis of 5-diazouracils leads to 1,2,3-triazoles in 60–90% yield.[40]



Conversions of 5-diazouracils into compounds of the 1,2,3-triazole series are used in nucleic acid chemistry.[37,41]

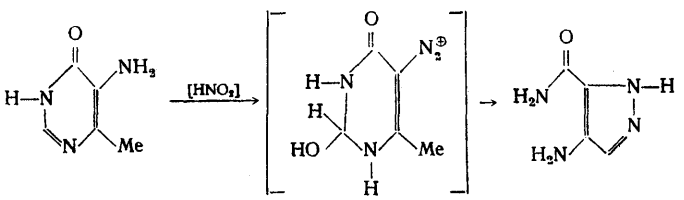
4-Substituted 5-amino-1-(β-cyanoethyl)-1,6-dihydropyrimidine-6-thiones, in contrast to 6-alkylthio derivatives are converted by diazotisation into 5-amino-1,2,3,thiadiazoles.[34,35,42]



R=Cl (a), OMe (b)

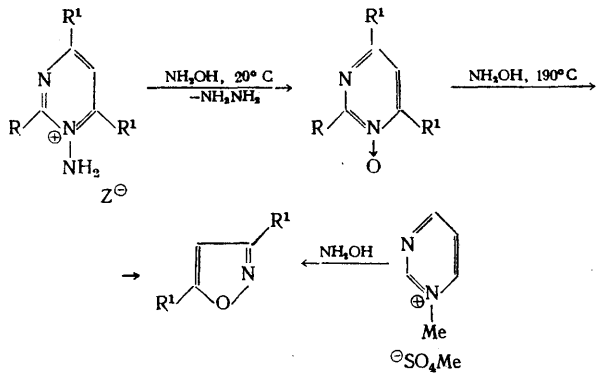
R^1=CN, R^2=CHO (a), R^1=COH, H; R^2=COOMe (b)

In the case of 5-amino-4-methyl-6-oxo-1,6-dihydropyrimidine, the acyclic intermediate formed under conditions of diazotisation is cyclised to a pyrazole derivative owing to the presence of the methyl group.[34,35]

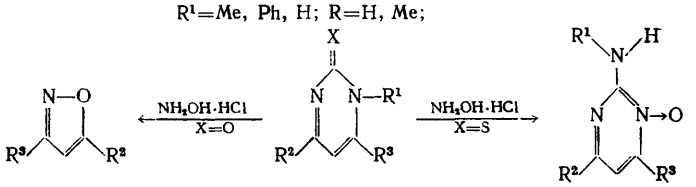


N-Dinitrophenylpyridinium salts give pyridine *N*-oxide on interaction with hydroxylamine through a glutaconic aldehyde derivative.[7,13]

Interaction of pyrimidine compounds with hydroxylamine usually leads to an isoxazole derivative or pyrimidine *N*-oxide.[43–45]

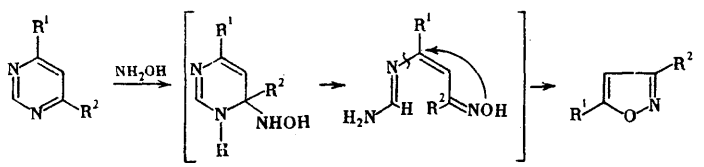


R^1=Me, Ph, H; R=H, Me;

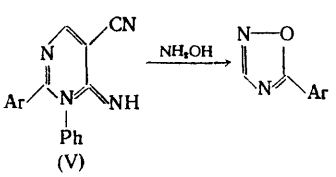


R^1, R^2, R^3=Me, Ph, Ar.

It is assumed that in these reactions hydroxylamine is added at the 1,6-position of the pyrimidine nucleus after which the ring breaks. The intermediate cyclises to an isoxazole compound containing the C(4)–C(5)–C(6) fragment of the initial pyrimidine.[43]

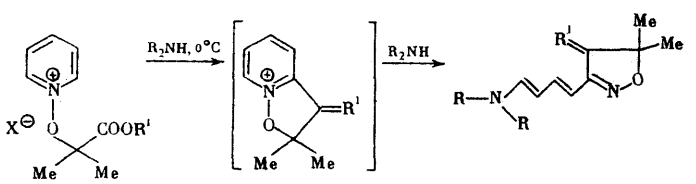


Pyrimidine compound (V) is converted under the action of hydroxylamine into a 1,2,4-oxadiazole derivative.[10,46]



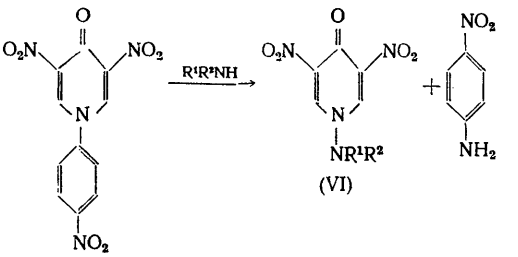
(V)

Alkoxypyridinium salts are recyclised in methanol with amines into isoxazole derivatives.[47] The isolation of the bicyclic intermediate from the reaction mixture confirmed the proposed scheme.[47]



R^1 = OEt(a), Ph(b), R^1 = O(a), Ph, OH(b) R^1 = O(a), Ph, OH(b)

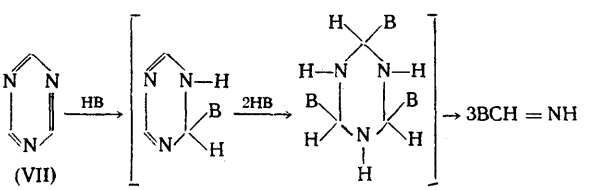
When 3,5-dinitro-1-(4-nitrophenyl)pyrid-4-one reacts with amines recyclisation occurs with the formation of 4-nitroaniline and the corresponding 1-amino substituted pyridone (VI).[48] This reaction (55–100% yield) is used for replacing amino groups in amino acids. The free amino acid is obtained by reacting (VI) with stronger bases. Racemisation of the amino acid was not observed.[49]



(VI)

R^1, R^2 = $-(CH_2)_5-$; R^1 = H, R^2 = Alk, amino acid.

In contrast to pyridines and pyrimidines unsubstituted 1,3,5-triazine (VII) is able to add up to three molecules of nucleophile with the formation of an adduct which is decomposed into three molecules of amine by the following scheme.[50]

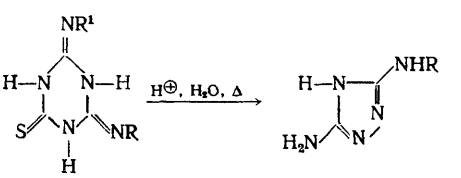


(VII)

HB – nucleophile

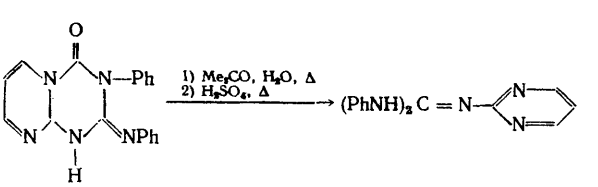
The ability of (VII) to be decomposed into three fragments by the action of nucleophiles is used in various syntheses for introducing a methylenimine group.[51–56]

Unsymmetrically substituted 1,3,5-triazines may be recyclised in a more complex manner under the action of nucleophilic reagents.[57]



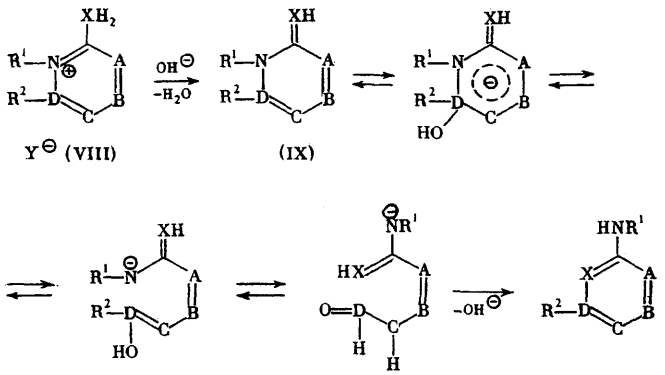
R = H, Ph; R^1 = H, NH.

Condensed pyrimido[1.2a]1,3,5-triazines are split in a stepwise manner. Initially the pyrimidine ring is cleaved on boiling in aqueous acetone and a 2-acroleylamino-1,3,5-triazine derivative is obtained. Boiling in sulphuric acid causes opening of the 1,3,5-triazine ring and splitting away of the acroleylamino residue. Subsequent cyclisation leads to a pyrimidine derivative.[58]



III. The Dimroth and Kost–Sagitullin reactions

Rearrangements are often observed in the reaction of nucleophiles with electron-deficient nitrogen-containing rings. A general mechanism for this is given in the scheme.[59,60]



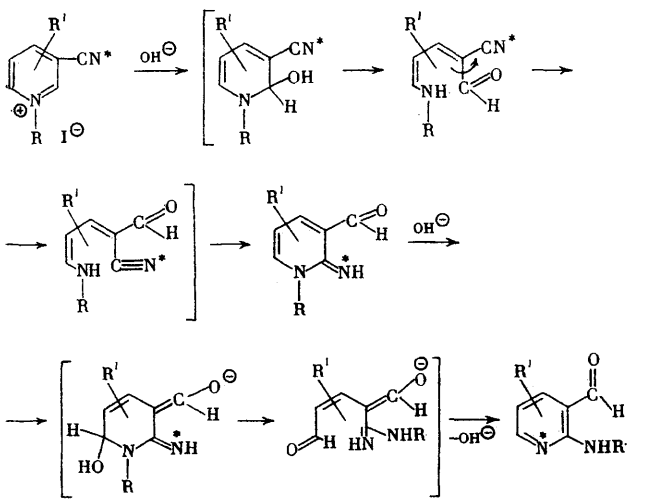
$Y^{\ominus}$ (VIII) (IX)

X, A, B, C, D = N or CH.

A quaternary salt of the heterocycle (VIII), its anhydro base or imino form (IX) adds nucleophile (hydroxyl ion, amine or hydroxylamine) and is converted into a new heterocyclic system. If a new C–N bond is formed as a result of recyclisation the reaction is called a Dimroth rearrangement.[61] If a new C–C bond is formed on recyclisation and the obtained heterocycle contains one atom of nitrogen less than the initial (VIII) such a rearrangement is called a Kost–Sagitullin rearrangement.[8,60] The presence of labile exocyclic α-atoms of hydrogen is one of the conditions for these reactions.[59]

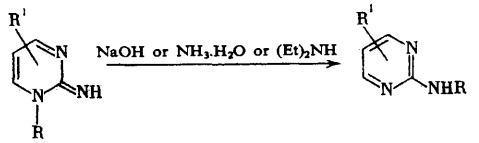
The Kost–Sagitullin rearrangement is characteristic of pyridinium and pyrimidinium salts[9] and the Dimroth reaction is a feature of pyrimidines and 1,3,5-triazines[61] but is rarely met in pyridines.[62]

1-Alkyl-3-cyanopyridinium iodides are converted in alkaline solution first into derivatives of 1-alkyl-2-aminopyridine which are recyclised once more into 2-alkylaminopyridines. To detect the indicated conversions it was helpful to introduce ^{15}N into the cyano group of the initial pyridine and study the subsequent behaviour of the label.[62]



R = Me, R^1 = H(a); R = Et, R^1 = 5-Me(b); N* – ^{15}N-labelled atom.

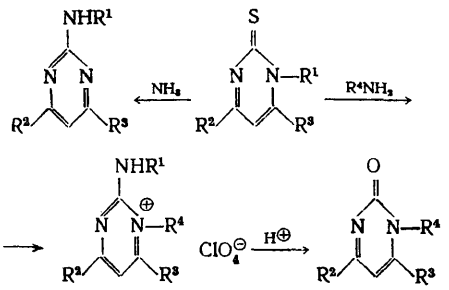
The Dimroth rearrangement for pyrimidines usually takes place in protic solvents in the presence of base. 1-Substituted 2-amino-1,2-dihydropyrimidines take part in it particularly readily[61] and are converted into 2-alkylaminopyrimidines.



R = Alk, CH_2COOEt; R^1 = Alk, Hal, NO_2, $N(Et)_2$.

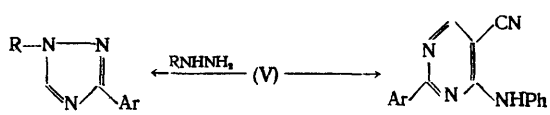
The reaction does not take place in aprotic solvents, a change of protic solvent may influence the course of the rearrangement.

1,4,6-Trisubstituted 2(1H)-pyrimidinethiones react with ammonia in a sealed tube by a type of Dimroth rearrangement. The presence of perchlorate anion is necessary for the analogous rearrangement with primary amines. The resulting salts are readily hydrolysed by acid to 2-pyridones.[63]



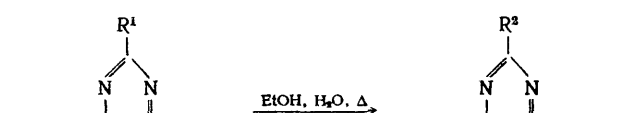
R^1, R^3 = Me, Ar, Ph; R^2 = Me; R^4 = Alk.

Reaction of pyrimidines (V) with guanidine, ethylenediamine or thiosemicarbazide gives 2-aryl-5-cyano-4-phenylaminopyrimidines, the products of Dimroth rearrangement.[10,46] When a bulky substituent is present in the nucleophile recyclisation leads to a 1,2,4-triazole derivative.[10,46]



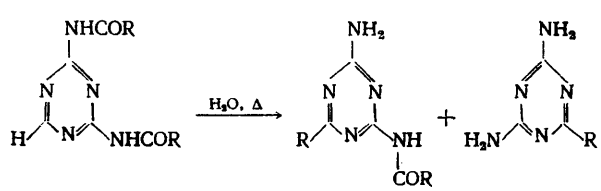
R = Ar, Ph, H

2,4-Diacylamino-1,3,5-triazines undergo a Dimroth rearrangement on heating in aqueous alcoholic solution.[64,65]



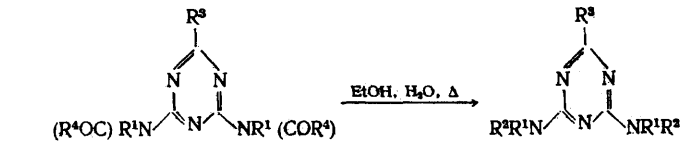
R^1 = H, Me; R^2 = Ph, Ar.

Two products are formed in the case of aliphatic *N*-acyl residues[66] and the processes proceed more rapidly than for the corresponding aromatic acyl derivatives.



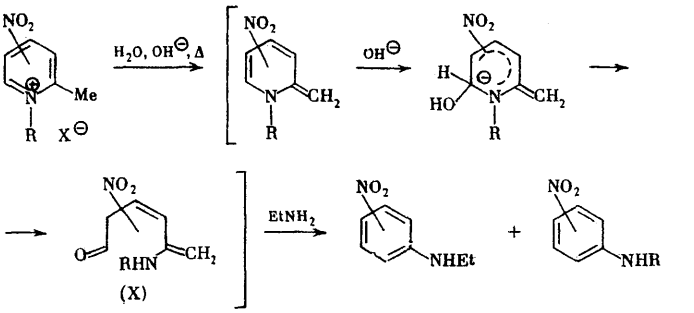
R = Alk

2,4-Di-(*N*-alkyl, *N*-acylamino-1,3,5-triazines undergo a double Dimroth rearrangement on boiling in aqueous alcohol.[67] The reaction proceeds twenty times more slowly with *N*-alkylated *N*-acylaminotriazines than with *N*-unalkylated compounds.



R^1 = Alk; R^2 = H; R^3, R^4 = Me, Ph, Ar, H.

The simplest example of a Kost–Sagitullin rearrangement is the recyclisation of pyridines[68] and their quaternary derivatives[69–74] on heating in aqueous solutions of ammonium salts and alkali to give substituted alkylanilines.



Recyclisation is assisted by electron-accepting substituents in positions 3 and 5 of the pyridine ring,[69–72] by the presence in the α-position to nitrogen of groups capable of deprotonation with the formation of anhydro bases and by the presence of amine as cyclising agent in the reaction mixture.

If the substituents in the amine and at nitrogen of the pyridinium ring are different then transamination at the stage of the acyclic intermediate (X) and the formation of several recyclisation products is possible.

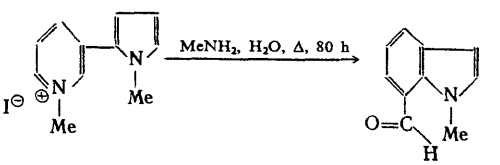
The presence of groups with labile hydrogen atoms at positions 2 and 6 of the pyridine leads to the formation of two anhydro bases (XI) and (XII) and as a result two isomeric anilines (XIII) and (XIV) are generated in the presence of methylamine.[70,72,73]

The ratio of (XIII) and (XIV) is determined by the degree of preference of attack of hydroxyl ion on the initial pyridine at the position *para* to the nitro group compared to the formation of *ortho* isomer (XII). However transamination of the acyclic intermediate (XI) is hindered. Consequently *para* isomer (XIV) predominates in the transamination products (except when R = Me).[75]

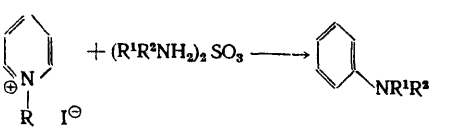
When the chain length of the *N*-alkyl substituent in the pyridinium salts reaches C_{12}, in the author's opinion, micelle formation takes place in the aqueous solution in which the pyridine bases are disposed on the micelle surface.[76,77] As a result the approach of water molecules to the recyclisable product and ring opening are facilitated and the approach of amine is hindered and transamination practically does not occur.

The Kost–Sagitullin rearrangement is also used for introducing an aromatic residue into other heterocycles[78–81] and the preparation of aromatic amines.[8,82–88]

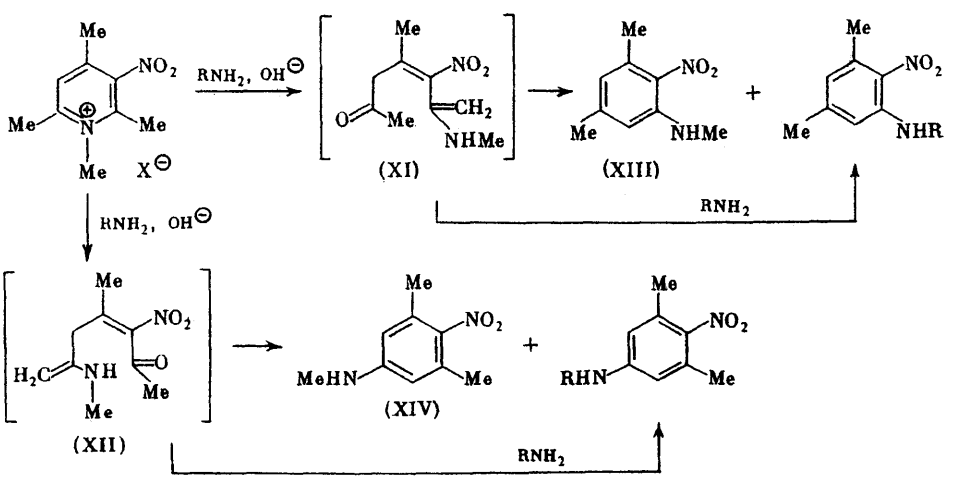
Thus heating nicotine methiodide at 150 °C with methylamine leads to recyclisation to 7-formyl-1-methylindole.[79]



Alkylpyridinium salts form arylamines under the conditions of the Kost–Sagitullin reaction.[82]

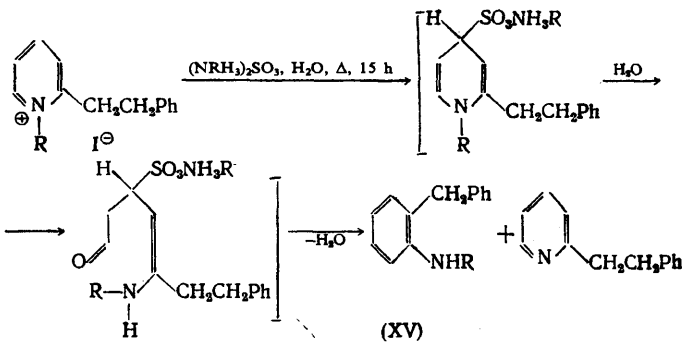


R, R^1, R^2 = Alk.

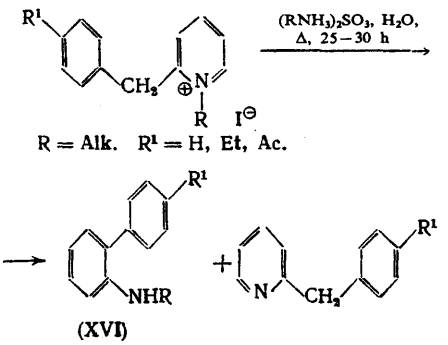


R = Alk

Similarly 2-(2-phenylethyl)pyridinium salts form *ortho*-alkylaminodiphenylmethanes (XV).[83,84]



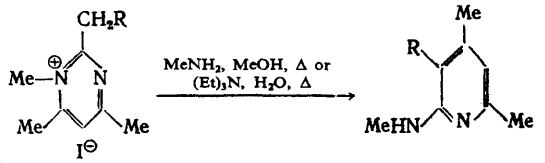
Benzylpyridinium salts form 2-aminobiphenyls (XVI).[85,86]



N-Dealkylation products are formed in these reactions together with (XV) and (XVI).[83–86]

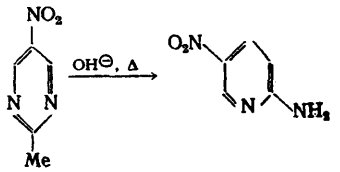
Transamination may occur at the ring opening stage if the R substituent in the pyridinium salt and in the alkylamine sulphite are different. Yields of biphenyl recyclisation products (XVI) are reduced with increasing volume of the *N*-alkyl group, or with the introduction of substituents into the α and β positions of the pyridine nucleus which hinders the addition of sulphite anion, or by introducing electron-donating residues into the phenyl nucleus impeding intramolecular cyclisation of intermediates.

Pyrimidinium salts readily add nucleophiles under conditions of the Kost–Sagitullin reaction and are converted into α-aminopyridine derivatives.[89]

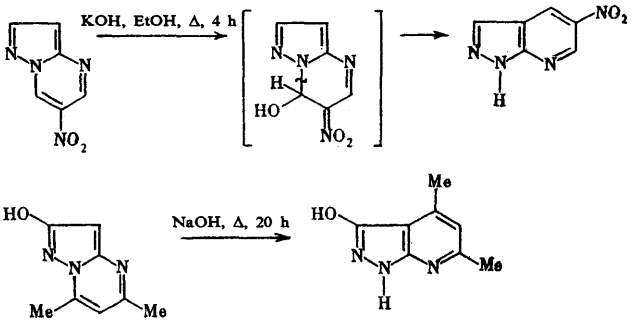


R = Ph, COOEt

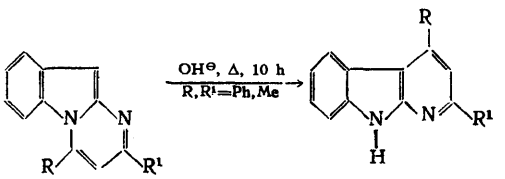
A nitro group in the pyrimidine ring facilitates these reactions and recyclisation of 2-methyl-4-nitropyrimidine is possible without obtaining the quaternary salt.[90]



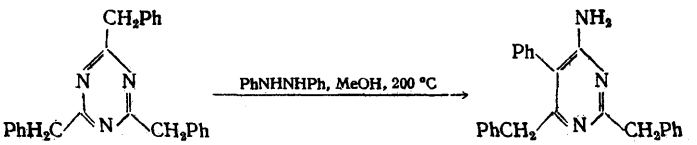
Condensed systems such as pyrazolo[1,2a]pyrimidines are recyclised into pyrazolo[3,4b]pyridines on heating with alkali. The presence of a nitro group in the starting material facilitates the reaction.[91]



Pyrimido[1,2a]indoles are converted into α-carbolines on boiling in alkali.[92]

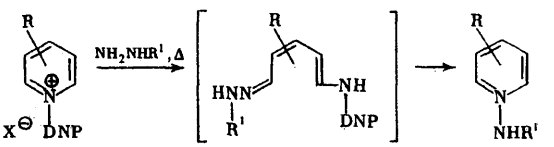


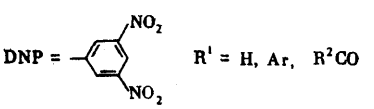
The Kost–Sagitullin rearrangement recalls the conversion of 2,4,6-tribenzyl-1,3,5-triazine into a pyrimidine derivative on heating with hydrazobenzene in methanol.[93]



IV. Recyclisations during hydrazinolysis

The interaction of pyridines, activated by donating-accepting substituents or transformed into quaternary salts, with hydrazine[7,13] proceeds with recyclisation of the pyridinium ring into an *N*-aminopyridinium ring.



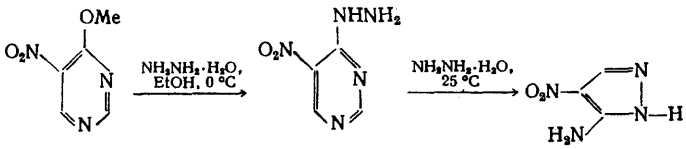


Many studies have been devoted to the hydrazinolysis of pyrimidine derivatives[35,90,94–104] mainly to pyrazoles[90,94–104] and to 1,2,4-triazoles.[35,95,102]

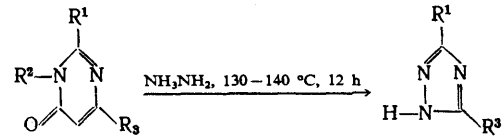
If there are substituents in the pyrimidine ring capable of interacting with hydrazine then at low temperature (<0 °C) hydrazinopyrimidines are formed.[94,96,99,101] and on increasing the temperature (occasionally to room)[99] and using an excess of

hydrazine, addition of one further molecule of hydrazine to the pyrimidine[96,99,101] and recyclisation were observed.

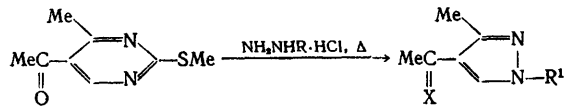
4-Methoxy-5-nitropyrimidine forms 4-hydrazino-5-nitropyrimidine with hydrazine hydrate in alcohol at 0 °C, which at room temperature and with an excess of hydrazine is converted into 3-amino-4-nitropyrazole.[96]



Analogous reactions proceed above 100 °C in the absence of the nitro group.[102]



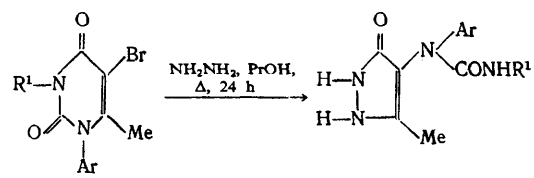
Heating 5-acetyl-4-methyl-2-methylthiopyrimidine with hydrazine hydrochlorides leads to pyrazole derivatives.[101]



R = H, Me, Ph, C(=NH)NH$_2$, CONH$_2$, CSNH$_2$;

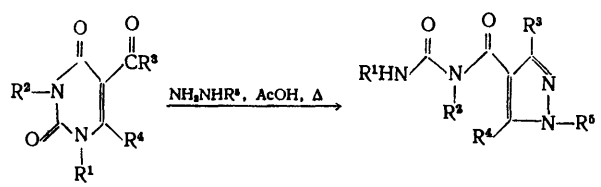
X = O, NH$_2$; R^1 = R, H

On heating 1,3-disubstituted 1-aryl-5-bromo-6-methyluracils with hydrazine in isopropanol they recyclise into 4-substituted 3-pyrazolones.[97,98]



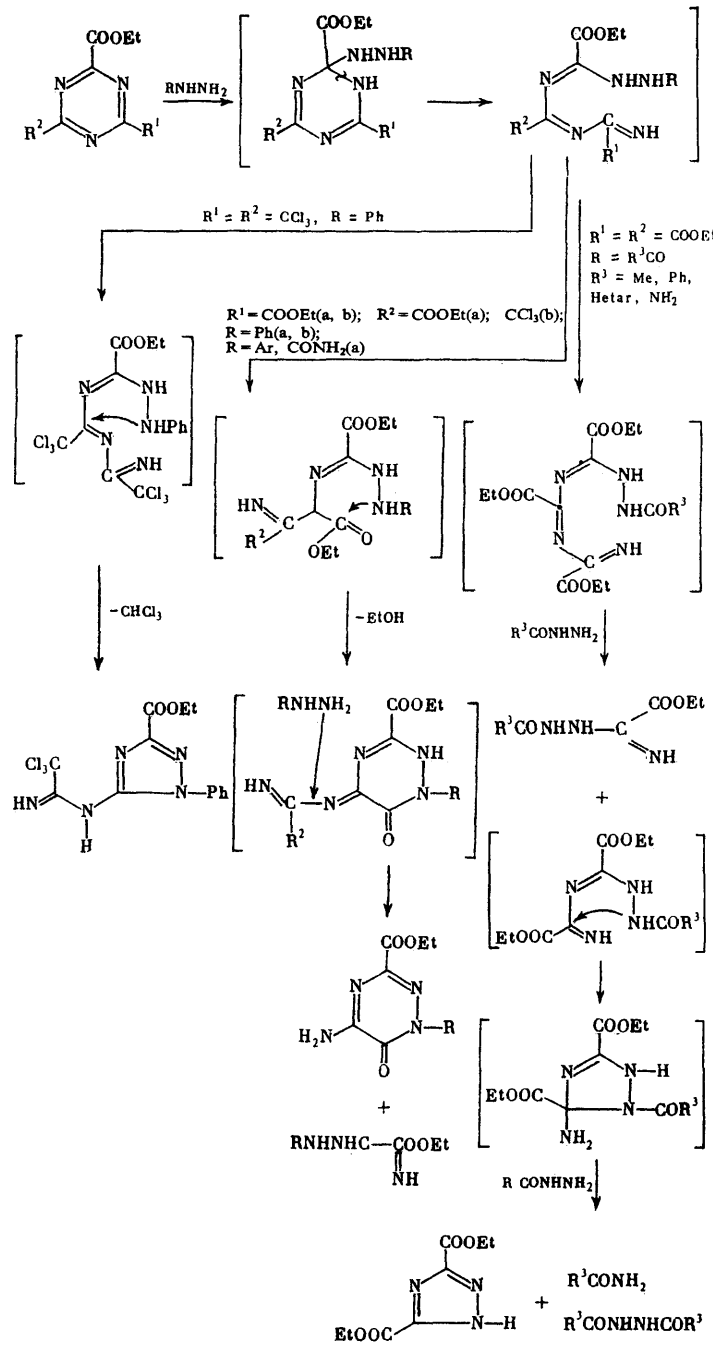
R^1 = Alk, —CH$_2$—CH=CH$_2$.

Hydrazinolysis of uracil derivatives in acetic acid also leads to pyrazoles.[99,100]



R^1, R^4 = H, Me, Et; R^2, R^3, R^5 = H, Me.

By reaction with aryl-, acylhydrazines, semicarbazide or thiosemicarbazide 2,4,6-triethoxycarbonyl-1,3,5-triazines are converted into derivatives of 1,2,4-triazine or 1,2,4-triazole depending on the nucleophilicity of the hydrazine derivative nitrogen atoms. Acyclic products were also isolated from the reaction mixture the formation of which is in agreement with the proposed scheme.[105–109] The conversion of 1,3,5-triazines containing both trichloromethyl and ethoxycarbonyl groups goes by a similar scheme under the action of phenylhydrazine.[109] On reducing the nucleophilicity of the hydrazine (isoniazide) the reactions with 1,3,5-triazines containing ethoxycarbonyl and trichloromethyl groups did not go.



V. Reactions with alkali metal amides in liquid ammonia

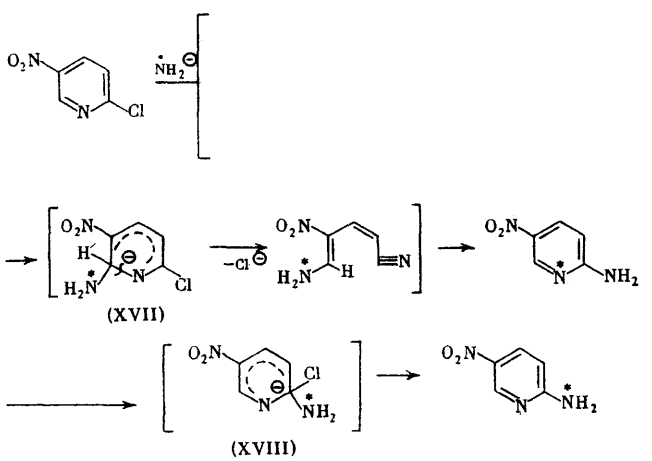
The reaction of nitrogen-containing heterocycles with potassium amide in liquid ammonia has been studied principally by van der Plas.[110,111,113,115–131] Depending on the structure of the

starting material and the concentration of potassium amide conversions may proceed both by an S_N(AE) and by an S_N(ANRORC) mechanism.

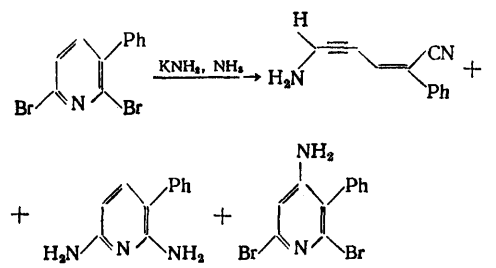
If the reaction is accompanied by recyclisation then the product may be both the initial ('degenerate recyclisation')[6] and a transformed heterocycle. Degenerate recyclisations were detected with an ^{15}N label in the potassium amide or in the heterocycle.[104,115–119,126,131]

The reaction of pyridine with potassium amide in liquid ammonia may proceed by an S_N(AE) mechanism (Chichibabin amination)[132] or with recyclisation of the pyridine nucleus.[110–115] In both cases the process starts with the formation of a σ complex of pyridine with amide anion. Electron-accepting substituents in the pyridine molecule facilitate the formation of a σ complex, opening of the ring and subsequent recyclisation.

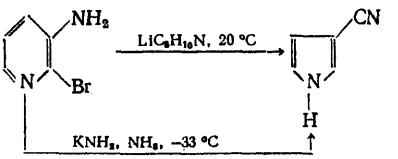
2-Chloro-5-nitropyridine forms two σ complexes (XVII) and (XVIII) with amide anion, the nitro group in the *ortho* position enables breaking of the C(2)–N(1) bond and the resulting intermediate is cyclised to 2-amino-5-nitropyridine. The second σ complex (XVIII) splits off chloride anion and is also converted into 2-amino-5-nitropyridine.[110] To discriminate between the resulting pyridines was possible with the aid of potassium amide labelled with ^{15}N. Steric hindrance occurred in the formation of σ complex (XVIII) consequently 75% σ complex (XVII) was formed.



It was possible to form three products under the same conditions from 2,6-dibromo-3-phenylpyridine, viz. an acyclic compound, 2,6-diamino-3-phenylpyridine [(S_N(ANRORC) mechanism] and 4-amino-2,6-dibromo-3-phenylpyridine [S_N(AE) mechanism].[111]

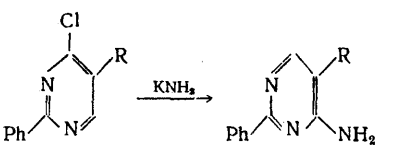


3-Amino-2-bromopyridine is converted into 3-cyanopyrrole with potassium amide in liquid ammonia at −33 °C or with lithium piperidinide at 20 °C.[114]



In pyrimidines as in pyridines the interaction with potassium amide in liquid ammonia may occur with a 'degenerate recyclisation'.[115–127] The course of the reaction is principally determined by the structure of the initial pyrimidine.

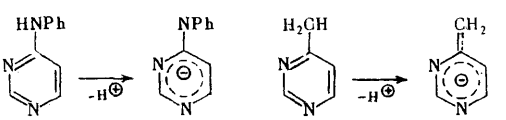
5-Substituted 4-chloro-2-phenylpyrimidines form σ complexes with amide anion at positions 4 and 6, position 2 is sterically hindered. On breaking the pyrimidine ring bonds C(4)–C(5) and C(5)–C(6) respectively were severed.[120]



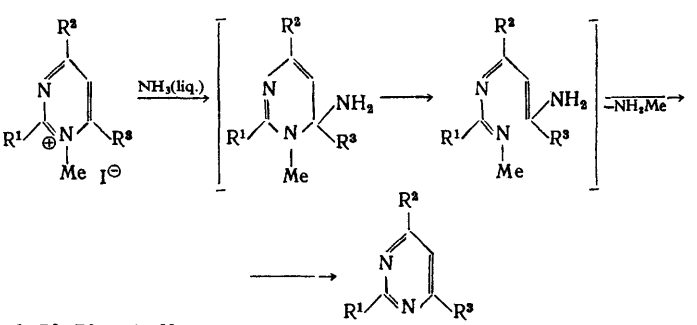
R = OMe, SMe, Ph, OEt.

In order that the interaction of pyrimidines with amide anion should go by an S_N(ANRORC) mechanism it is necessary to observe the following conditions.[120–123] There must be the possibility of forming a σ complex able to open the pyrimidine ring. With unsubstituted pyrimidines a σ complex is formed at position 2. In substituted pyrimidines several σ complexes may be formed.[120,122,123] For 2-fluoro substituted pyrimidimes the splitting away of fluoride ion occurs after the formation of σ complex with amide anion at position 2 and the reaction goes by the S_N(AE) mechanism.[123]

Substituents at positions 4 and 6 of the pyrimidine nucleus must not have an acidic proton capable of forming stable anions of type (XIX) and (XX) hindering attack of the nucleophile.[121]



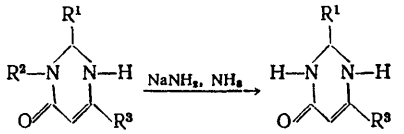
Dealkylation of *N*-alkylpyrimidinium salts in liquid ammonia may occur at an S_N(ANRORC) mechanism.[79,124]



R¹, R², R³ = H, Me.

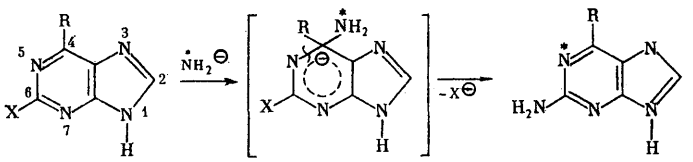
6-Ethoxy-1,3-diethyl-4-oxo-3,4-dihydropyrimidinium tetrafluoroborate is dealkylated in liquid ammonia to 3-ethyl-6-ethylamino-4-oxo-3,4-dihydropyrimidine.[125]

The interaction of 4,6-disubstituted 3-alkyl-2-pyrimidones with sodium amide in liquid ammonia also leads to dealkylation at nitrogen.[102]



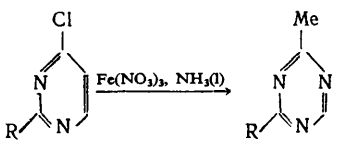
R^1 = iso-Pr, Ph; R^2 = H, Me, Et; R^3 = Me, Et.

The reaction of 2-substituted purines with potassium or sodium amides in liquid ammonia is accompanied by the formation of a complex at position 6 with subsequent conversion of the pyrimidine nucleus.[126,127] If position 6 in the purine is occupied by a methyl group amination goes by an S_N(AE) mechanism.



X = Hal, SMe; R = H, Me.

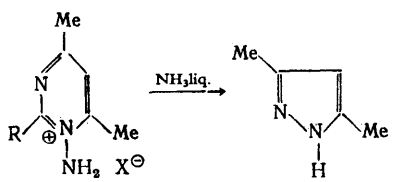
!,3,5-Triazines[128] and five-membered nitrogen-containing rings[129] may be obtained by the recyclisation of pyrimidines in liquid ammonia.



R = Alk; Ph, N(Me)$_2$

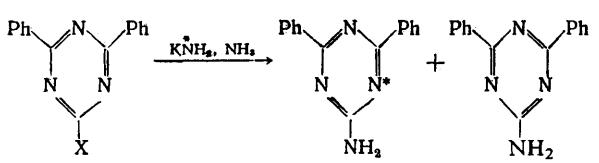
It was established by ^{14}C labelling that the C(5)–C(6) bond in the pyrimidine ring was severed.[128]

N-Aminopyrimidinium salts were converted into liquid ammonia into 3,5-disubstituted pyrazole.[129]



R = H, Me.

The interaction of substituted 1,3,5-triazines with potassium amide in liquid ammonia may be accompanied by a 'degenerate recyclisation'. Whether the amination reaction has an S_N(ANRORC) or S_N(AE) mechanism depends on the potassium amide concentration and the nature of the leaving group.[130,131]



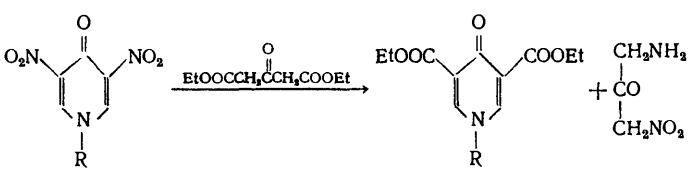
X = H, Cl, SMe.

VI. Conversions with CH-acids and ambident nucleophiles

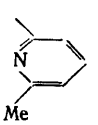
It was considered previously that the general mechanism for the reaction of nitrogen-containing π-deficient heterocycles with anions of CH-acids or ambident nucleophiles consisted of addition of anion to the heterocycle with the formation of a Meisenheimer complex, opening of the heterocycle and closure of a new ring with replacement of a portion of the ring atoms by a residue of the ambident nucleophile or CH-acids [S_N(ANRORC) mechanism]. The formation of a Meisenheimer complex is facilitated if the heterocycle is activated by an electron-accepting substituent.

Recent work has shown that the formation of bridge structures is occasionally possible for ambident nucleophiles on reaction with a heterocycle. In some cases these structures have been successfully established.[11,134,135,151,159,161,169] To establish non-cyclic intermediates and σ adducts is more difficult since they are unstable and their further conversion by ring opening and rapid recyclisation are thermodynamically favourable.

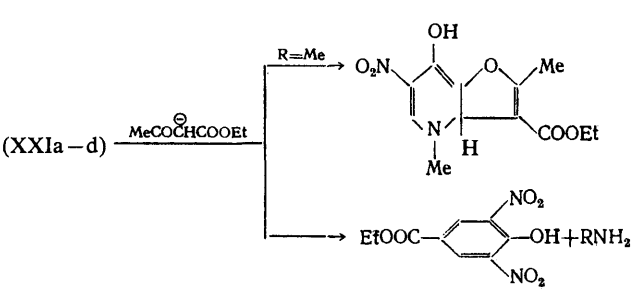
1-Substituted 3,5-dinitro-4-oxo-1,4-dihydropyridines (XXIa–e) with acetonedicarboxylic acid diethyl ester form 1-substituted 3,5-diethoxycarbonyl-4-oxo-1,4-dihydropyridines (58–85% yield) and 3-amino-1-nitropropan-2-one.[133,134]



(XXI а — д)

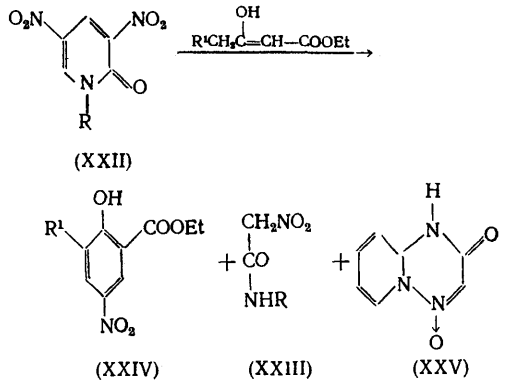
R = Me (a), 3-Py (b), 4-Py (c),  (d), H (e).

The interaction of (XXIa–d) with the sodium derivative of acetoacetic acid ester in alcohol depends on substituent R at the nitrogen atom in (XXIa–d). The reaction product is a furano-[2,3b]pyridine for the electron-donating R = Me (XXIa). In the case of electron-accepting substituents (XXIb–d) the reaction product was 4-hydroxy-3,5-dinitrobenzoic acid ethyl ester.[134]



The interaction of 1-substituted 3,5-dinitro-2-oxopyridines (XXII) with the sodium derivative of acetoacetic ester (R^1 = H) or acetonedicarboxylic acid ethyl ester (R^1 = COOEt) depending on the character of the substituents R and R_1 leads to *N*-substituted

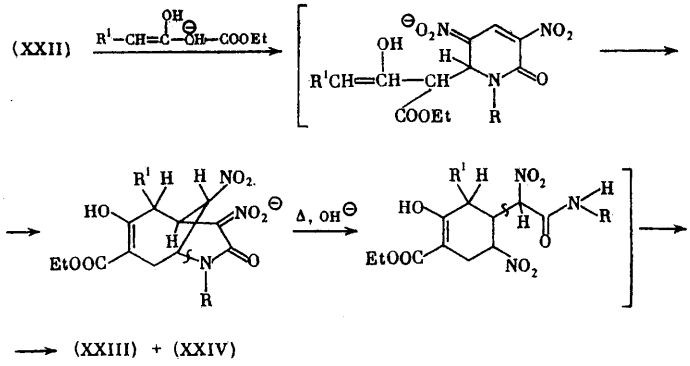
α-nitroacetamide (XXIII), a derivative of 5-nitrobenzoic acid ethyl ester (XXIV) and bicyclic derivatives (XXV).[133–137]



(XXII) (XXIV) (XXIII) (XXV)

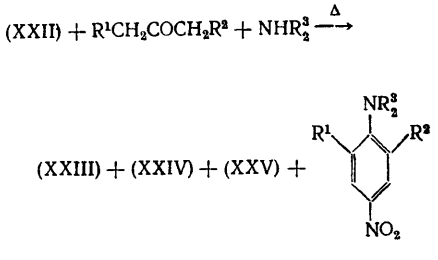
R = Me, CH_2Ar, CH_2Hetar, H, OMe, 2-Py; R^1 = H, COOEt.

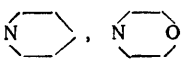
Conversion of pyrid-2-ones (XXII) to *para*-nitrophenols (XXIV) may go through an anionic σ adduct and then through a bicyclic derivative according to the scheme.[134–137]



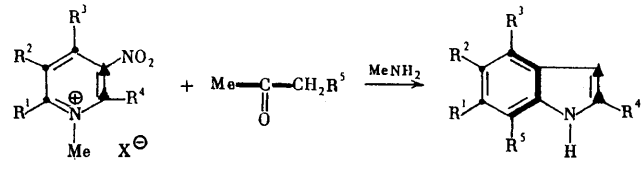
(XXII) → (XXIII) + (XXIV)

On reacting pyrid-2-one (XXII) with ketones in the presence of amines condensation of amine with ketone and further reaction of the resulting activated enamine with pyridone (XXII) may occur. Consequently *N*-substituted *para*-nitroaniline is present in the reaction products in addition to *para*-nitrophenol (XXIV).[137]

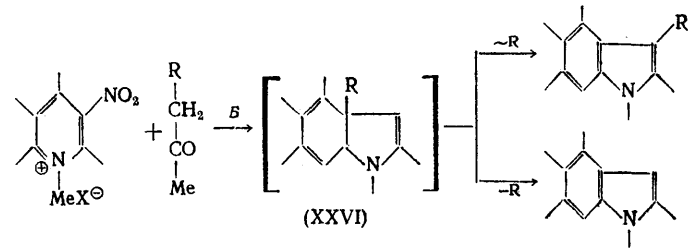


R^1, R^2 = H, Me, COOEt; NR^3_2 = 

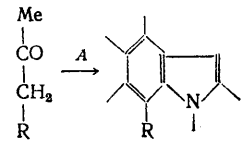
It was discovered recently tht 3-nitropyridinium salts are converted into indole derivatives on reaction with ketones in the presence of amines.[138,139] A specially developed spectroscopic procedure made it possible to establish the structure of the products formed and to suggest structural rules for the construction of the indole molecules ('diazine' process).[140]



The reaction seemingly begins with condensation of ketone or ketimine with the pyridinium salt and the formation of a bicyclic derivative in which the C(3)–C(4) and C(6)–N(1) bonds of the pyridinium nucleus are broken. A three carbon fragment of the ketone is introduced between the fragments of the pyridine ring. The proposed scheme was confirmed by the detection by chromatomass spectrometry of the two different directions (A and B) for the process linked with the orientation of the ketone on reaction with the pyridinium salt.[141]



(XXVI)

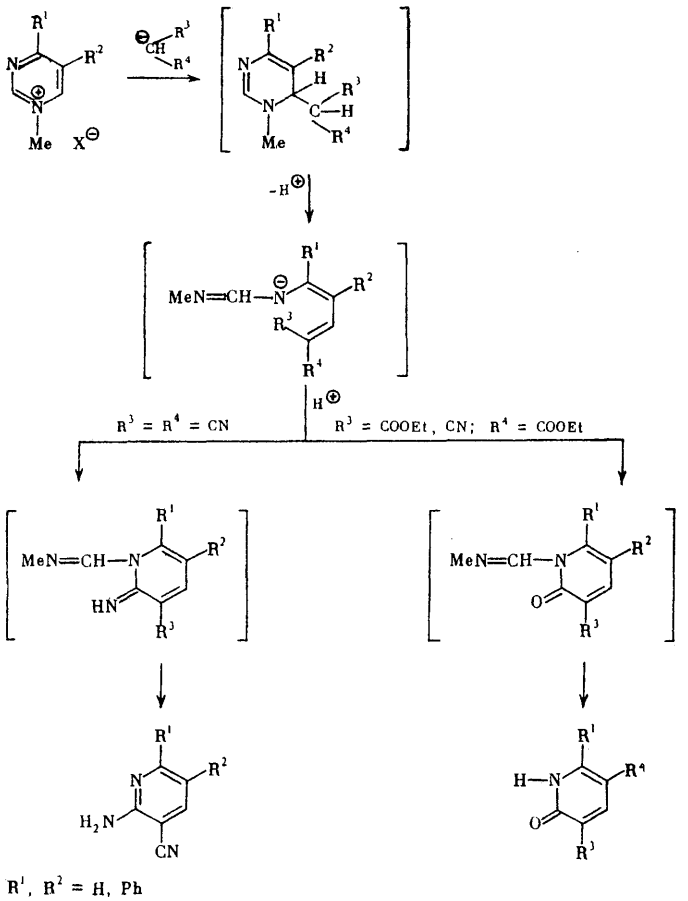


Route A leads to an indole of normal structure. In the case of route B intermediate (XXVI) may be aromatised by migration of R or by its elimination.

The use of prepared ketimines (in place of a mixture of ketone and amine) and polar aprotic solvents in the reaction improves yields (up to 80%) and simplifies the isolation process of the indole.[142,143]

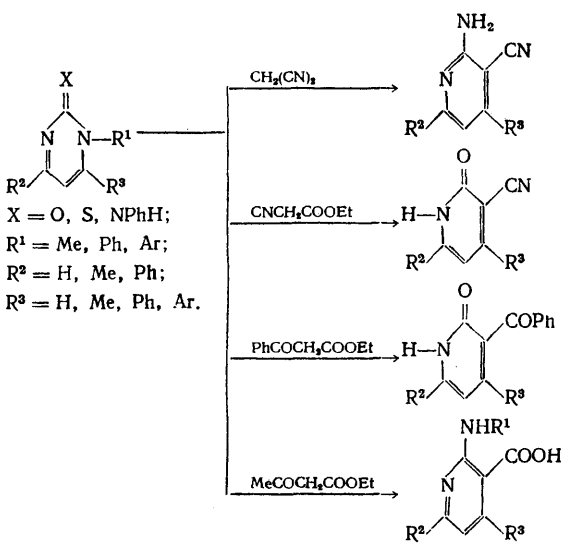
Many recyclisations of the pyrimidine ring on reaction with CH-acids and ambident nucleophiles are known.[144–172] To facilitate these reactions the pyrimidine derivatives are usually converted to quaternary salts,[145] and are then converted into substituted pyridines on reaction with the sodium derivatives of malonic ester, malondinitrile or cyanoacetic ester by replacement of the N(1)–C(2) fragment of the pyrimidinium system by a two-carbon fragment of the CH-acid. In the case of cyanoacetic ester closing of the acyclic intermediate as shown in the scheme goes through the ester and not

through the cyano group.[145]



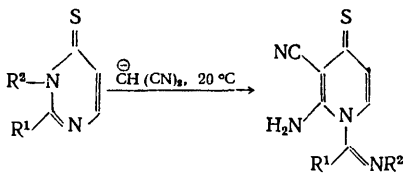
R^1, R^2 = H, Ph

The interaction of 2,4,6-trisubstituted 2,3-dihydropyrimidines with compounds having an active methylene group at room temperature in the presence of sodium ethoxide leads to pyridines.[146] In this the C(6)–N(1) bond in the initial pyrimidine is broken and yields of the pyridine derivative are determined by steric hindrance in the formation of a σ complex with the CH-acid at position 6 of the pyrimidine ring.



X = O, S, NPhH;
R^1 = Me, Ph, Ar;
R^2 = H, Me, Ph;
R^3 = H, Me, Ph, Ar.

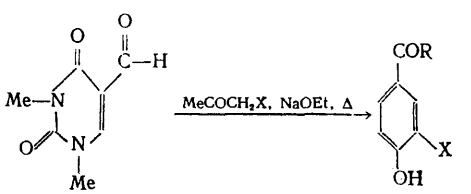
Interaction of 2,3-disubstituted 4-thio-3,4-dihydropyrimidines with malondinitrile in the presence of sodium ethoxide also goes with the formation of pyridine derivatives. Because of steric factors the CH-acid is added at C(4) of the pyrimidine nucleus and the C(4)–N(3) bond of the pyrimidine ring is broken.[147]



Three atoms of the pyrimidine ring may be replaced by three atoms of the nucleophilic reagent.[144,148–153]

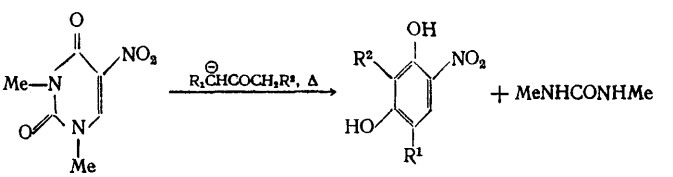
If the N(1)–C(2)–N(3) fragment of the pyrimidine nucleus is replaced by a C–C–C or C–C–N residue from an ambident nucleophile then benzene derivatives are formed in the first case[144,148–152] and pyridine derivatives in the second.[144,148,151,153]

On boiling 5-formyl-1,3-dimethyluracil with CH-acids in alcoholic sodium ethoxide derivatives of *p*-hydroxybenzoic acid are formed.[148,149,152]



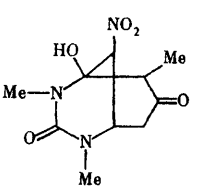
X = COMe, $CONH_2$, Ph, COOEt; R = OEt, NHMe.

1,3-Dimethyl-5-nitrouracil with ketones in boiling alcoholic alkali is recyclised to nitroresorcinol derivatives.[150]



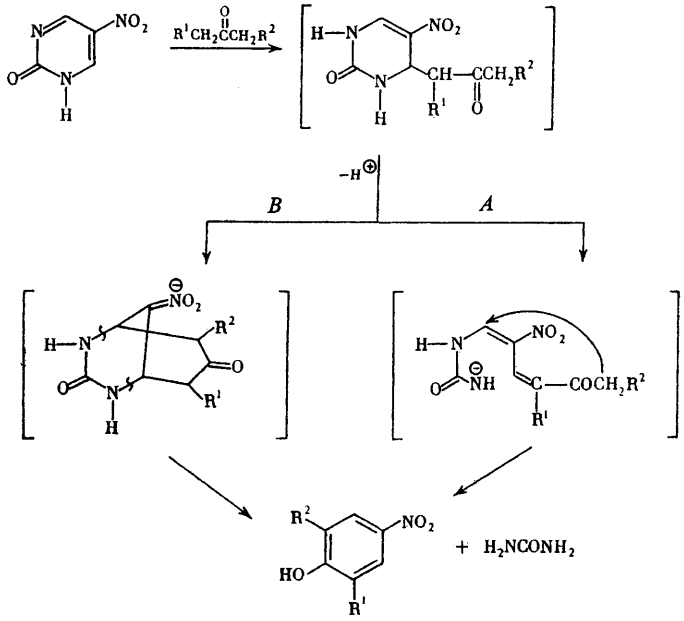
R^1 = COOEt, H, Me; R_2 = H

With unsymmetrically substituted ketones (R_1 = Me, R^2 = H) a mixture of two final products is formed because of the possibility of forming σ complexes at the different CH-groups.[150] A bicyclic product was isolated from the reaction mixture in the case of butanone.

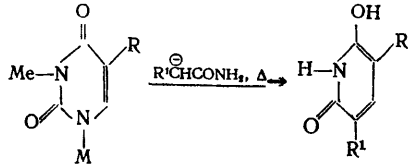


Similar bicyclic structures were successfully established in the reaction of ketones with 5-nitro-2-oxo-1,2-dihydropyrimidines. The final products of this reaction were *para*-nitrophenol derivatives.[151] Conversion of the pyrimidinium nucleus into benzene occurs in two directions, an S_N(ANRORC) (route *A*) and through

the formation of a bicyclic structure with subsequent splitting away of a urea derivative (route *B*).[151]

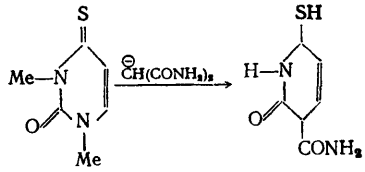


Reaction of 1,3-dimethyluracils with α-substituted acetamides in alcoholic sodium ethoxide leads to pyridine derivatives.[148,149,152,153]

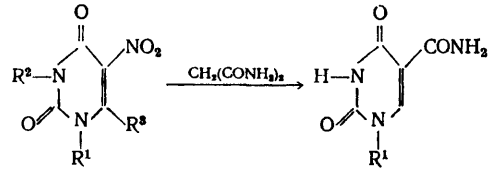


R = H, Me, CN, F,  ; $R^1 = CONH_2$, **CN**, COMe, Ph.

A 2-hydroxy-6-mercaptonicotinamide is formed from 1,3-dimethyl-6-thiouracil by an analogous reaction.[153]

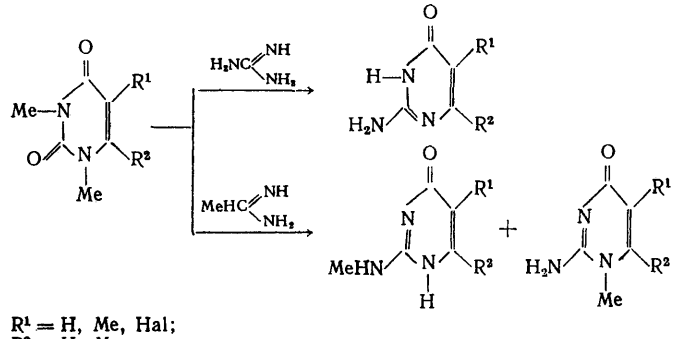


Reaction of 5-nitrouracils with malondiamide in alcoholic sodium ethoxide leads to 5-carboxamidouracils.[154,155] In this case the C–C–N residue of the nucleophile replaces C(5)–C(4)–N(3) of the pyrimidine ring. The reaction does not take place when the substituents at the uracil nitrogen atoms $R^1 = R^2 = H$ since the anionic form of the initial uracil is not able to add nucleophile.

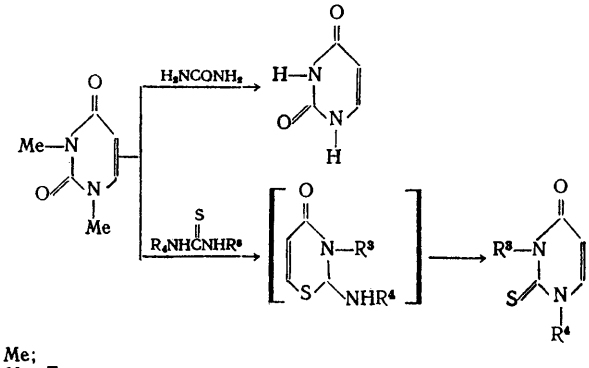


R^1, $R^3 = H$, Me, C_6H_{11}; $R^3 = H$, Me.

A 'degenerate recyclisation' occurs when the N(1)–C(2)–N(3) fragment of the pyrimidine is replaced by the N–C–N fragment of the nucleophile. Derivatives of guanidine, urea and thiourea are used as nucleophiles. Similar conversions of pyrimidine bases are used in nucleic acid chemistry.[144,148,149,156,157]



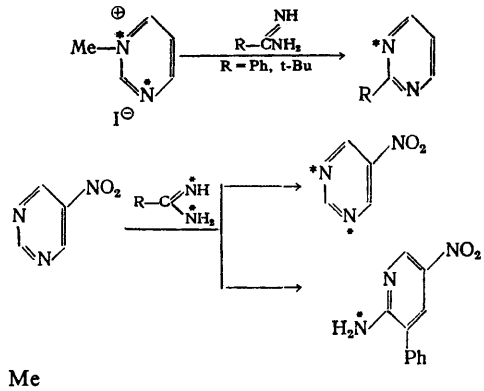
$R^1 = H$, Me, Hal;
$R^2 = H$, Me



$R^3 = H$, Me;
$R^4 = H$, Me, F.

6-Methyluracil derivatives (R^2 = Me) do not react with ureas due to the impossibility of forming a Meisenheimer complex at position 6. Electron-accepting substituents at position 5 of the pyrimidine facilitate the reaction.[157]

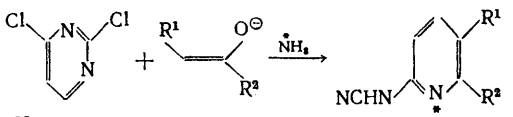
Recyclisation of quaternary salts or pyrimidines activated by a nitro group goes ambiguously with the formation of pyrimidines and pyridine (demonstrated by ^{15}N NMR).[158–161]



R = Ph, t-Bu, Me

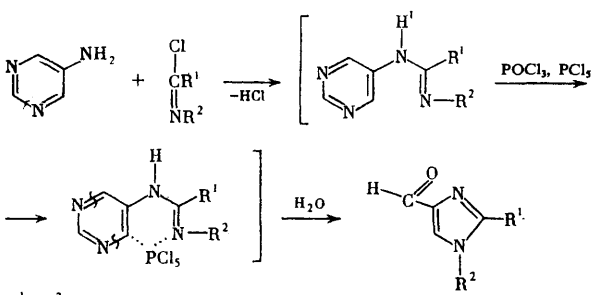
Reaction of 2,4-dichloropyrimidine with the potassium enolates of ketones in liquid ammonia leads to recyclisation to 2-cyano-pyridine. The N(1)–C(2)–N(3) fragment of the pyrimidine nucleus is

replaced by the C–C fragment of the ketone and a nitrogen from the ammonia (demonstrated by ^{15}N NMR).[162]



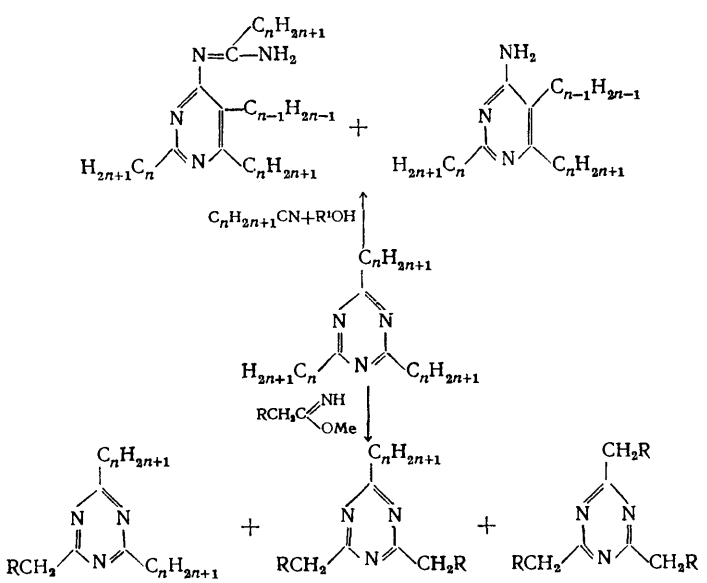
R^1, R^2 = Alk, H.

The conversions of pyrimidines considered above by reaction with ambident nucleophiles occur with the formation of six-membered heterocycles. Reaction of 5-aminopyrimidine with imidoyl chlorides in the presence of phosphorus oxychloride or pentachloride leads to 1,2-disubstituted 5-formylimidazole.[163] Phosphorus oxychloride or pentachloride is necessary to activate the nitrogen atoms, initially the side chain nitrogen is activated and then that in the pyrimidine ring.[163]



R^1, R^2 = H, Alk, Ph

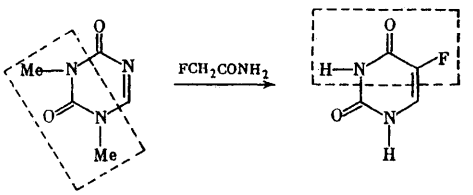
The reaction of 2,4,6-trialkyl-1,3,5-triazines with nitriles in alcohol at 100–150 °C under pressure is seemingly effected by conversion of nitrile into iminoether which replaces a portion of the triazine molecule. The reaction product may react with a further molecule of imidate and it is possible to obtain a completely transalkylated triazine.[164] A reaction was also possible under the same conditions in which pyrimidine derivatives are formed.[165]



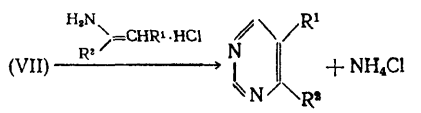
n = 1, 2; R = Me, Ph, Ar, Hetar; R^1 = H, Me, Et.

A similar process was evidently observed in the reaction of 2,4,5-trisubstituted 1,3,5-triazines with ammonia and nitriles in the presence of catalyst.[166]

With 1,3-dimethyl-5-azauracil fluoroacetic acid amide replaces the N–C–N fragment of the 1,3,5-triazine by a C–C–N fragment of the nucleophile with the formation of 5-fluorouracil. The reaction goes by an S_N(ANRORC) mechanism.[167]

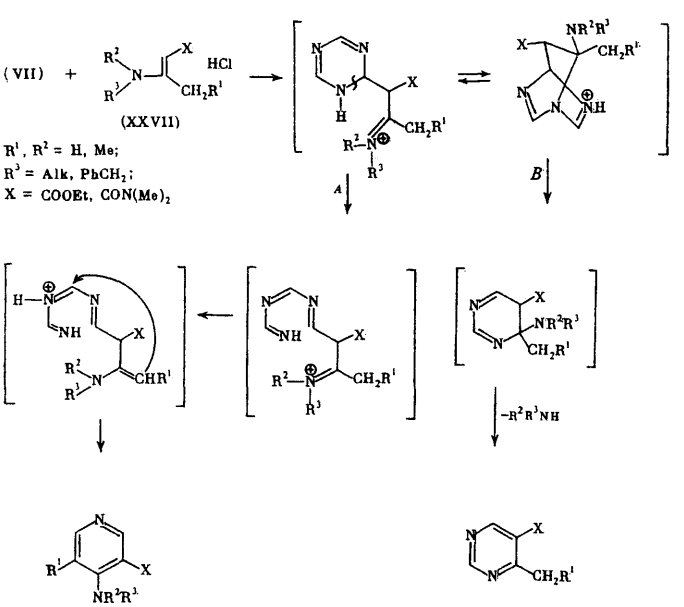


Heating 1,3,5-triazine (VII) in acetonitrile with an activated enamine hydrochloride leads to a 4,5-disubstituted pyrimidine.[168]



R^1 = Alk; R^2 = COOEt, MeCO.

However on boiling (VII) in acetonitrile with enaminoketone (XXVII) pyrimidine derivatives constitute a reaction by-product (5–10% yield). The formation of 4-aminopyridines containing electron-accepting substituents is the main direction (30–45% yield).[169] The ability of (XXVII) to insert three of its carbon atoms into the pyridine ring is unusual. An *N*-phenyl substituent in (XXVII) impedes the reaction.



It was proposed that (VII) is protonated by the action of (XXVII) hydrochloride, its nucleus is activated towards nucleophilic attack by the β carbon atom of (XXVII) and simultaneously towards recyclisation into a bicyclic adduct. An equilibrium mixture of intermediates is present in the mixture at the first stage of the reaction of (VII) and (XXVII). One of them is converted by route *A* [S_N(ANRORC) mechanism] into a pyridine derivative and the other proceeds by a reverse Diels–Alder reaction by route *B* with the formation of a pyrimidine derivative.[169]

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Generation and reactions of silylenes in the gas phase

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ABSTRACT. Results of the investigations in recent years on the gas phase thermal reactions of both inorganic and organic silylenes have been correlated. Particular attention has been paid to the sources used for generation of these unstable intermediates and also to methods of obtaining and to the properties of cyclic silylenes.

The bibliography contains 62 references.

Contents

I. Introduction 531
II. Reactions of silylenes generated from substituted di- and polysilanes 531
III. Generation of dihalosilylenes on thermal decomposition of 1,1-dichloro(difluoro)-silacyclopent-3-enes and 1,1-dichloro(difluoro)-silacyclohexa-2,4-dienes 535
IV. Methods of obtaining and reactions of cyclic silylenes 535

I. Introduction

Much attention has been paid in recent years to the study of the synthetic possibilities of using unstable derivatives of divalent silicon, viz. the silylenes, in gas phase pyrolytic reactions and also to the search for accessible sources of these molecules.[1–16] Recent achievements in the chemistry of gas phase reactions of silylenes, which are most interesting in the authors' view, have been correlated and systematised in the present work.

II. Reactions of silylenes generated from substituted di- and polysilanes

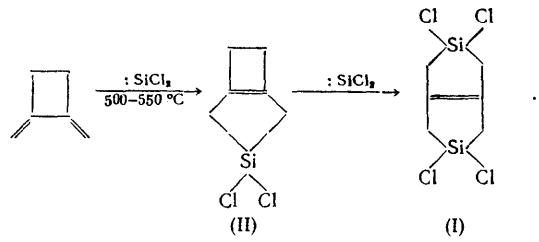
1. Addition of silylenes to multiple bonds

Thermal decomposition of various substituted disilanes in the gas phase is one of the most convenient and sufficiently general methods of generating silylenes. It was shown recently[17,18] that methyl and methylphenyl substituted cyclohexasilanes are also sources of organic silylenes in thermal reactions.

(a) Inorganic silylenes

Spectrometric investigations of gas phase reactions of addition of dichlorosilylene, generated from hexachlorodisilane, to the multiple bonds of acyclic and cyclic dienes have permitted on the one hand a significant broadening of the synthetic possibilities of the gas phase technique of thermal cyclisation and on the other the obtaining of data on the relative reactivity of various classes of compounds towards $:SiCl_2$.

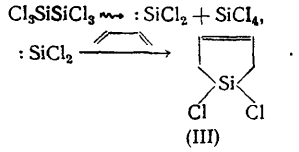
Addition of $:SiCl_2$ to such a specific diene system as 1,2-dimethylenecyclobutane leads to the formation of an unsaturated bicyclic compound with two silicon atoms in the ring, viz. 3,3,7,7-tetrachloro-3,7-disilabicyclo[3.3.0]oct-1,5-ene (I).[19] The sequence of conversions may be represented by the scheme:



(II) (I)

Seemingly the first product of addition of $:SiCl_2$ to the initial diene is the heterocycle (II) which then undergoes further insertion of $:SiCl_2$ into a C–C bond of the strained four-carbon ring. At a reagent ratio of Si_2Cl_6 : diene equal to 2 : 1 the yield of heterocycle (I) was 70%. On reducing the quantity of $:SiCl_2$ in the reaction mixture by half the yield of heterocyclic compounds fell to 25–30%.

A new method of generating dichlorosilylene by decomposing hexachlorodisilane radiochemically has been proposed.[20] 1,3-Butadiene was used as active intercepting agent for dichlorosilylene.



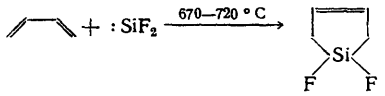
(III)

Under static conditions using an ELV-8 electron accelerator with a 30 kV beam as source of ionising radiation 1,1-dichloro-1-silacyclopent-3-ene (III) was formed at lower temperatures (200 –300 °C) than without irradiation (> 350 °C).

There is significant practical interest in the thermal interaction of perchloropolysilanes containing hydrochloropolysilanes with various acyclic 1,3-butadienes leading to the formation in almost quantitative yield of 1,1-dichloro-1-silacyclopent-3-ene or derivatives of it.[21] This method permits the use of still residues formed in processes of hydrochlorinating silicon as a source of dichlorosilylene in place of hexachlorodisilane.

The interception reaction of the highly reactive monomeric :SiF_2 in gas phase pyrolysis of hexafluorodisilane in an excess of 1,3-butadiene has recently been effected successfully.[22]

$$Si_2F_6 \rightarrow : SiF_2 + SiF_4,$$

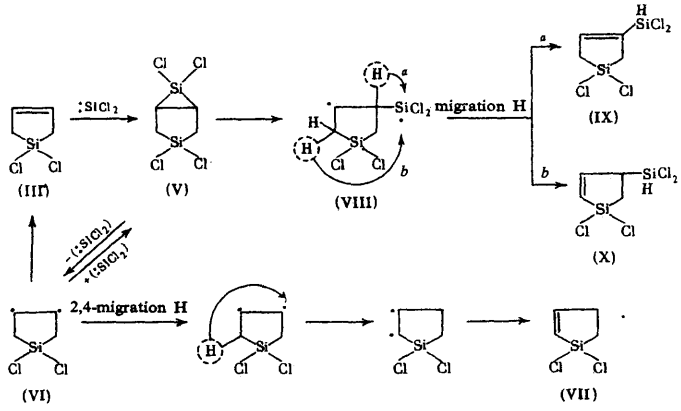


(IV), 56—75% .

The process was carried out in a flow system with a reactant contact time of 0.01—0.02 sec.

Study of the gas phase thermal isomerisation of 1,1-dichloro-1-silacyclopent-3-ene (III) into 1,1-dichloro-1-silacyclopent-2-ene in the presence of added hexachlorodisilane showed the essential role of dichlorosilylene in this process.[23] Thus isomerisation of the heterocycle in the absence of a source of :$SiCl_2$ began only at 480—500 °C but introduction of added hexachlorodisilane (4.86—16.4 mol%) into the reaction zone accelerated the isomerisation of compound (III) and reduced the temperature for the start of reaction to 380—400 °C. With an increase in the quantity of added hexachlorodisilane, and therefore an increase in :$SiCl_2$ concentration in the reaction zone, the extent of isomerisation of heterocycle (III) was increased. To explain the accelerating influence of dichlorosilylene a scheme was proposed for the isomerisation with the initial addition of :$SiCl_2$ to the olefinic bond of 1,1-dichloro-1-silacyclopent-3-ene (III).

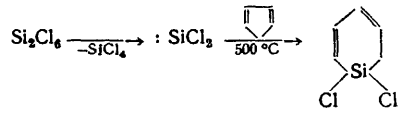
Scheme 1



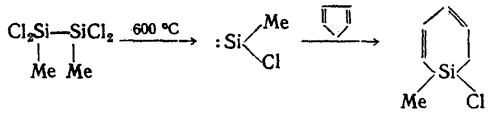
On adding :$SiCl_2$ to the multiple bond of heterocycle (III) the bicyclic compound (V) is formed which has an unstable silacyclopropane ring the decomposition of which at both intracyclic Si—C bonds leads to biradical (VI) which is subsequently converted either to the initial heterocycle (III) or (with 2,4 migration of hydrogen) to heterocycle (VII).

The proposed Scheme 1 is also in good agreement with the formation of dichlorosilyl substituted dichlorosilacyclopentenes in this reaction. Fission of one Si—C bond of the silacyclopropane ring of bicycle (V) leads to biradical (VIII) and then to a mixture of silyl-substituted heterocycles with Si—H bonds (IX) and (X) as a result of intracyclic hydrogen migration.

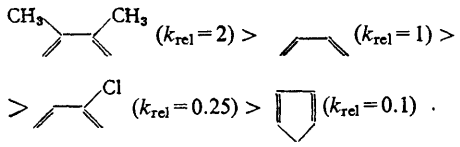
Such cyclic diene systems as cyclopentadiene (or its dimer) proved to be interesting subjects for studying the addition reaction. Reaction of hexachlorodisilane with cyclopentadiene leads to 1,1-dichloro-1-silacyclohexa-2,4-diene in 45—50% yield.



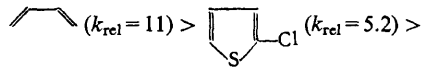
The procedure, published in our studies[2,3,5,6,24] on the thermal synthesis of this previously unavailable monocyclic silicon compound, has been reproduced repeatedly.[25,26] Thus Barton and Banasiak[27] synthesised 1-methyl-1-chloro-1-silacyclohexa-2,4-diene by thermal interaction of tetrachlorodimethyldisilane with cyclopentadiene.



A similar reaction has also been carried out in vacuum (650 °C, 10^{-2} Torr).[28] Communications have appeared recently for the first time on the relative reactivity of various classes of compounds towards :$SiCl_2$ generated thermally from hexachlorodisilane.[19,29,30] The following series of relative activities of various dienes for :$SiCl_2$ adding to multiple bonds has been established using competing reactions (flow reactor, 500 °C).[19,29]



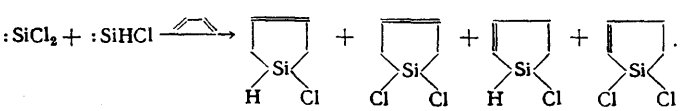
The relative reactivities of 1,3-butadiene, 2-chlorothiophen, chlorobenzene and hydrogen chloride towards :$SiCl_2$ have also been determined (flow reactor, 420—440 °C).[30]



$> C_6H_5Cl$ ($k_{rel} = 1$) < HCl ($k_{rel} = 0.33$) .

It follows from the obtained data that aromatic chlorides are poorer acceptors of :$SiCl_2$ than 1,3-butadiene. The least effective acceptor of dichlorosilylene proved to be HCl. Its reactivity was 30 times lower than that of 1,3-butadiene.

Hexachlorodisilane and its mono- and dihydro derivatives were formed on pyrolysis of trichlorosilane in the presence of added chloroform (quartz flow reactor, 450—600 °C, 1 mol% $CHCl_3$ relative to $HSiCl_3$).[31,32] Thus at 350 °C the content of tetrachloro-, pentachloro- and hexachlorodisilanes in the pyrolysate was ~15%, and of $SiCl_4$ 25%. It is possible that the decomposition products of chloroform are capable of forming these compounds. Interaction of dichloro- and chlorosilylenes generated from the disilanes indicated above with 1,3-butadiene yields a mixture of mono- and dichlorosilacyclopentenes.[32] The maximum overall yield of chloro-substituted silacyclopentenes (21% on initial trichlorosilane) was observed at 550 °C.



It should be mentioned that monochlorosilacyclopentenes (11%) are formed at a lower temperature (510 °C).

(b) Organic silylenes

Investigations carried out recently on the study of gas phase addition reactions of organic silylenes generated from various di-, poly- and cyclohexasilanes with organic substituents on the silicon atom encompass processes both at atmospheric pressure and at high vacuum. Mainly alkynes and conjugated dienes were used as active 'interceptors' of silylenes. The principal directions of the work were as follows. At the theoretical level kinetic data were obtained on gas phase reactions of the pyrolytic formation of silylenes and the mechanisms of the reactions involving them were studied. At the synthetic level new sources for generating organic silylenes have been sought.

Among the kinetic investigations which should be mentioned is the determination of rate constants and activation parameters for gas phase reactions for the pyrolytic formation of silylenes from 1,2-dimethoxytetramethyldisilane, methoxypentamethyldisilane, 1-methoxy-1-propyltetramethyldisilane and 1,2-dimethyldisilane (pyrolysis in a nitrogen stream, 304–450 °C, ~1000 Torr).[33] The reactions studied were first order with respect to disilane. The majority of experiments with disilanes were carried out in an excess of 1,3-butadiene as a trap for silylenes to suppress secondary reactions.

There are interesting data on the reaction mechanism for the addition of $:SiH_2$ generated on pyrolysis of disilane to ethylene.[34] The obtained results made it possible to consider the interaction of $:SiH_2$ with ethylene in the gas phase as a sequential stepwise process comprising the initial formation of a silacyclopropane intermediate and subsequent conversion of it either into the starting materials or into ethylsilylene and vinylsilylene.

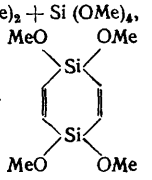
$$H_3SiSiH_3 \longrightarrow :SiH_2 + SiH_4,$$

$$:SiH_2 + CH_2{=}CH_2 \rightleftharpoons H_2C(CH_2)SiH_2 \longrightarrow C_2H_5\ddot{S}iH \quad / \quad \longrightarrow CH_2{=}CHSiH_3.$$

Hexamethoxydisilane is a good source of dimethoxysilylene in the gas phase.[35] Copyrolysis of this disilane with acetylene leads to 1,1,4,4-tetramethoxy-1,4-disilacyclohexa-2,5-diene in 56% yield.

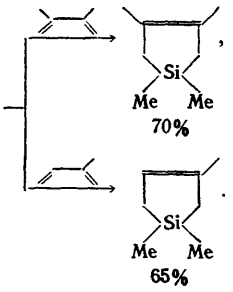
$$(MeO)_3SiSi(OMe)_3 \xrightarrow{\Delta} :Si(OMe)_2 + Si(OMe)_4,$$

$$:Si(OMe)_2 + CH{\equiv}CH \xrightarrow{370\ ^\circ C}$$

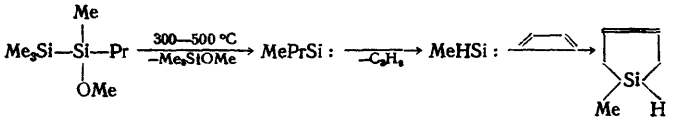


The addition of dimethylsilylene, generated thermally from 1,2-dimethoxytetramethyldisilane, to acyclic 1,3-dienes both at atmospheric pressure[36] and in vacuum[37] has been described.

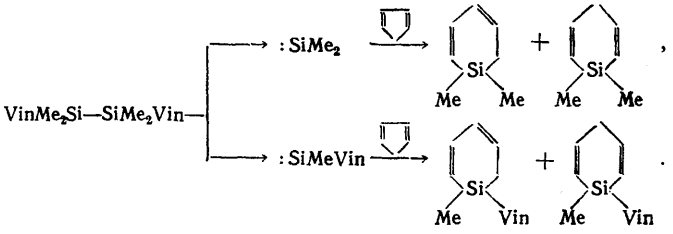
$$(MeO)\,Me_2Si{-}SiMe_2(OMe) \xrightarrow[-(MeO)_2SiMe_2]{450\ ^\circ C/2\ Torr} Me_2Si:$$



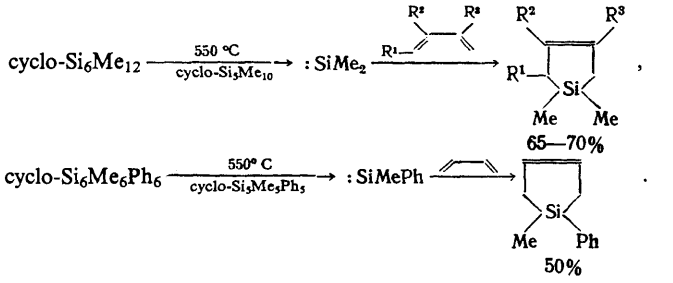
On pyrolysis 1-methoxy-1-propyltetramethyldisilane first forms PrMeSi: which is rapidly decomposed into MeHSi: and propene.[33,38]



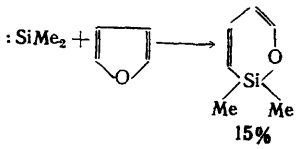
Thermal decomposition of 1,2-divinyltetramethyldisilane occurs non-selectively with the formation of dimethyl- and methylvinylsilylenes. Thus on copyrolysis of 1,2-divinyltetramethyldisilane with cyclopentadiene (650 °C, 10^{-2} Torr) substituted silacyclohexadienes are formed which are products of addition of both organic silylenes in approximately equal amounts.[39]

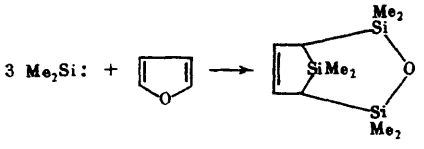


Studies on the thermal generation of dimethyl- and methylphenylsilylenes from dodecamethylhexaphenylcyclohexasilanes deserve special attention. These compounds were known to date only as photochemical sources of silylenes and were regarded, evidently due to their low volatility, as unsuitable for thermal reactions.[17,18] It has been shown that these cyclohexasilanes were capable of decomposing in the gas phase to the corresponding cyclopentasilanes and silylenes (flow reactor, 500–550 °C, contact time 40–60 sec).[17]



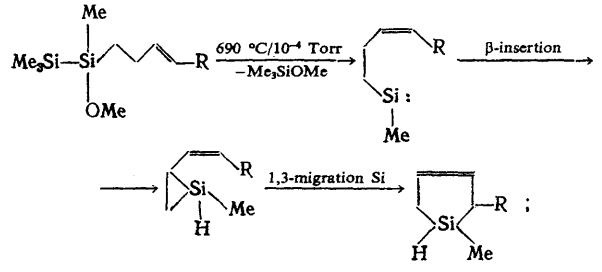
The formation of silylenes in these reactions was confirmed by the formation of silacyclopent-3-enes in the presence of 1,3-butadienes. The reaction of intercepting $:SiMe_2$, generated by pyrolysis of dodecamethylcyclohexasilanes, by furan (flow system, 500 °C) at atmospheric pressure has been studied for the first time.[18] Among the main reaction products 2,2-dimethyl-2-sila-1-oxacyclohexa-3,5-diene and the product of addition of three molecules of dimethylsilylene to furan were detected.



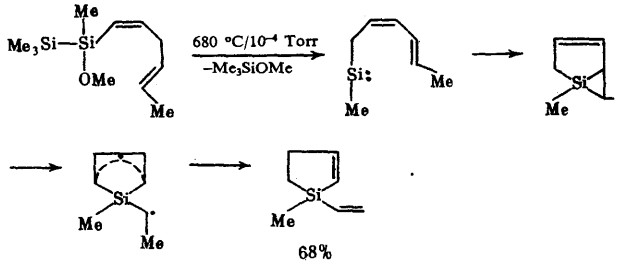


The reactions indicated above were carried out with dimethylsilylene generated by reaction of dimethyldichlorosilane with Na or K vapour at 400–500 °C.[18]

A new direction in the 'high temperature' chemistry of organic silylenes was the investigation of their intramolecular conversions. A method has been proposed for the intramolecular interception of silylenes generated from a series of methoxytetramethyldisilanes containing butenyl or pentadienyl groupings.[39] Reactions were carried out under high vacuum when generating such silylenes with a view to limiting the contribution of intermolecular reactions and secondary processes.

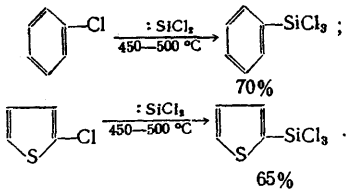


R = H, 56%; R = Me, 30%.

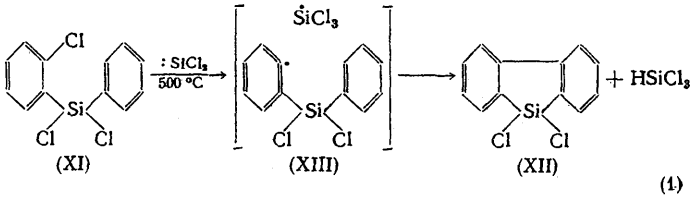


2. Gas phase thermal cyclisation reactions involving :$SiCl_2$

It was recorded previously that processes introducing dichlorosilylene, generated on pyrolysis of hexachlorodisilane, into a $C_{Ar}-Cl$ bond differ widely in selectivity.[2,4–6] They seemingly occur through a fission-recombination stage as in the reaction of singlet carbenes with the C–Cl bond.[40] Singlet :$SiCl_2$ removes a chlorine atom from the starting material with the formation of a pair of radicals. Recombination of the radicals with one another leads to the corresponding aryltrichlorosilane (separation of the radical pair is atypical for this interaction).



On studying the gas phase interaction of (*o*-chlorophenyl)phenyldichlorosilane (XI) with hexachlorodisilane (500 °C, reactant ratio 1 : 1) it was established unexpectedly that the main reaction product was 9,9-dichloro-9-silafluorene (XII) (90% yield).[41,42] The formation of a product of insertion of :$SiCl_2$ into a $C_{Ar}-Cl$ bond of the starting material did not occur in this case. It is interesting that compound (XI) in the absence of a source of dichlorosilylene was not subject to intramolecular dehydrochlorination with the formation of heterocycle (XII) in the range 400–550 °C and at 680 °C the yield of the latter did not exceed 18%.[43] The suggestion was made that the role of dichlorosilylene in the reaction studied is reduced merely to fission of a chlorine atom from the initial (XI) which permits intramolecular cyclisation, :$SiCl_2$ itself does not enter into the composition of the resulting reaction products.[3,5,6,43]



(1)

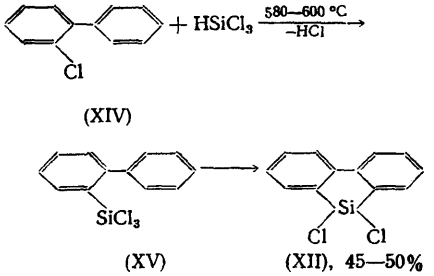
Evidently recombination of the radical pair did not occur in this case because of the increased tendency of radical (XIII) towards intramolecular cyclisation. It is extremely informative that the intermediate formation of a free radical with an unpaired electron solely at the ortho carbon atom, when the radical centre and the aromatic system are sterically close together, leads to an intramolecular cyclisation.

The interaction of (*p*-chlorophenyl)phenyldichlorosilane with hexachlorodisilane under the conditions studied leads only to the formation of (*p*-trichlorosilylphenyl)phenyldichlorosilane (30% yield).[42] *o*-(Trichlorosilylphenyl)phenyldichlorosilane, the product of inserting :$SiCl_2$ into the $C_{Ar}-Cl$ bond of compound (XI), was obtained by a different reaction;[43] up to 500–550 °C it did not undergo thermal conversions and at 680 °C cyclised by a different scheme with the formation of 9,9,10,10-tetrachloro-9,10-disila-9,10-dihydroanthracene (30% yield).

It should be noted that this gas phase reaction also occurs on using other sources of :$SiCl_2$, such as trichlorosilane and 1,1-dichloro-1-silacyclopent-3-ene in place of hexachlorodisilane.[42]

The observed gas phase reaction of dichlorosilylene has possibly no analogy in carbene chemistry and is the basis of a new general method of forming a series of silicon-containing heterocyclic systems.[3,5,6,44]

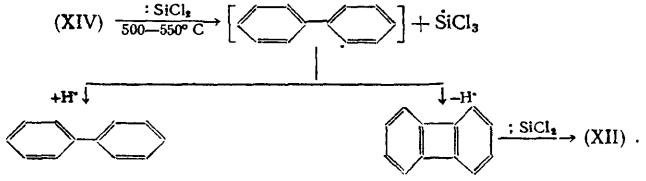
Recently this reaction was extended to ortho substituted aromatic hydrocarbons, particularly to *o*-chlorodiphenyl.[45] Formerly the high temperature synthesis of the heterocycle (XII) from *o*-chlorodiphenyl (XIV) was carried out in the presence of trichlorosilane.[46,47] It was shown that the initial step of the reaction was homolytic silylation of *o*-chlorodiphenyl (XIV) with subsequent intramolecular cyclisation of the resulting *o*-trichlorosilyldiphenyl (XV).



The significant role of temperature was noted. Heterocycle (XII) was formed only at 680–700 °C, at lower temperatures (580–600 °C) only the silylation product (XV) was detected.

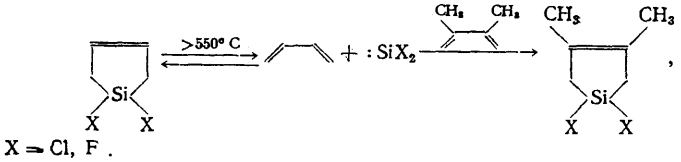
On thermal interaction of compound (XIV) with hexachlorodisilane heterocycle (XII) was formed under milder conditions and its yield was 75–80%. Diphenyl was the main byproduct. Compound (XV), which may be regarded as the product of inserting

$:SiCl_2$ into the $C_{Ar}-Cl$ bond of the initial *o*-chlorodiphenyl (XIV), was also isolated in insignificant yield (5–7%). A suggestion as to the possible cyclisation of compound (XV) at lower temperatures (500–550 °C) in the presence of hexachlorodisilane was not confirmed experimentally. These circumstances made it possible to propose another scheme for forming heterocycle (XII) through biphenylene in the reaction in question.



III. Generation of dihalosilylenes on thermal decomposition of 1,1-dichloro(difluoro)silacyclopent-3-enes and 1,1-dichloro(difluoro)silacyclohexa-2,4-dienes

The retrodiene decomposition of 1,1-dichloro- and 1,1-difluoro-1-silacyclopent-3-enes under high temperature conditions has been reported previously.[5,6,48]



X = Cl, F .

The use of the method of 'chemical trapping agents' has made it possible to obtain proof of the intermediate formation of dihalosilylenes in this reaction.

The formation of dichlorosilylene on pyrolysis of 1,1-dichloro-1-silacyclopent-3-ene (800–1400 K, pressure 10^{-1} to 10^{-2} Torr) was shown with the aid of IR spectroscopy in a solid argon matrix.[49] The direct mass spectrometric detection of primary products of vacuum pyrolysis of 1,1-dichloro- and 1,1-difluoro-1-silacyclopent-3-enes, viz. 1,3-butadiene and dihalosilanes was also effected with the aid of vacuum pyrolytic mass spectrometry.[50]

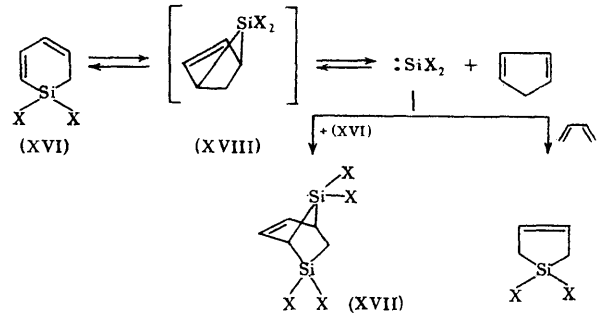
The formation of 1,1-dichloro-1-silacyclopent-3-ene in the gas phase from $:SiCl_2$ and 1,3-butadiene is thermodynamically favoured in the temperature range 300 to 1000 K.[51]

The successful demonstration of the thermal retrodiene decomposition of 1,1-dichloro-1-silacyclopent-3-ene forms a basis for the hypothesis that the gas phase interaction of $:SiCl_2$ with *symm-cis*-1,3-butadiene corresponds formally with the Diels–Alder reaction and therefore proceeds by a concerted 1,4-cycloaddition mechanism.

Pyrolysis of dihalo substituted silacyclopent-3-enes is an efficient means of generating not only dichloro- but also difluorosilylene. The preparation of monomeric $:SiF_2$ by other methods is very difficult.

1,1-Dichloro(1,1-difluoro)-1-silacyclohexa-2,4-dienes (XVI) are also capable of decomposing on pyrolysis (500–650 °C, flow system) by a retrodiene scheme with the formation of cyclopentadiene and dichloro(difluoro)silylene. The thermal decomposition of the difluoroderivative requires higher temperatures (600–650 °C).[29,52] The primary content of the pyrolysis products of these heterocycles has been studied by vacuum pyrolytic mass spectrometry.[50] Chemical proof has been obtained of the formation of dihalosilylenes on pyrolysis of these heterocycles. Thus copyrolysis of dienes (XVI) with 1,3-butadiene leads to the formation of the corresponding 1,1-dihalo-1-silacyclopent-3-enes. Pyrolysis of individual compounds (XVI) alone leads to the formation of cyclopentadiene and the 1,4-cyclo adduct (XVII) of $:SiX_2$ with the initial heterocycles probably by the following Scheme (Scheme 2).

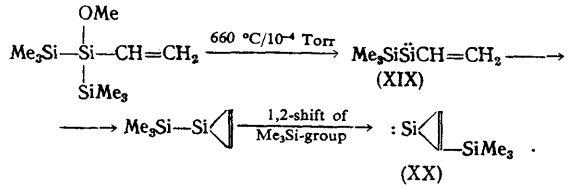
Scheme 2



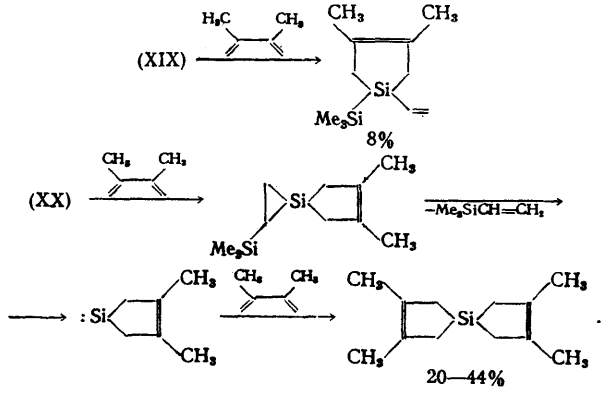
Mass spectrometric investigation of the decomposition routes of heterocycle (XVI) under electron impact also confirmed the possibility of forming the bicycle (XVIII) under these conditions.[53] The results obtained testify in favour of a 1,4-addition mechanism of $:SiCl_2$ to cyclopentadiene, however further study is required.

IV. Methods of preparation and reactions of cyclic silylenes

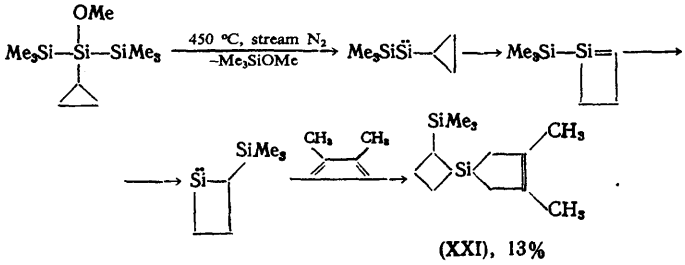
Two main routes for obtaining cyclic silylenes have been contemplated up to the present time: 1) thermal decomposition (at atmospheric pressure in a nitrogen stream or at high vacuum) of difficultly available organosilicon compounds undergoing complex intramolecular rearrangements[54–59] and 2) the use of gas phase dehalogenation of available dichloro substituted silacycloalkanes and silacycloalkenes with alkali metal vapour.[60–62] An interesting vinylsilylene intramolecular rearrangement was discovered on studying the pyrolysis of 2-methoxy-2-vinylhexamethyltrisilane.[54]



The existence of intermediates (XIX) and (XX) was confirmed by reaction of the initial trisilane with 2,3-dimethyl-1,3-butadiene.

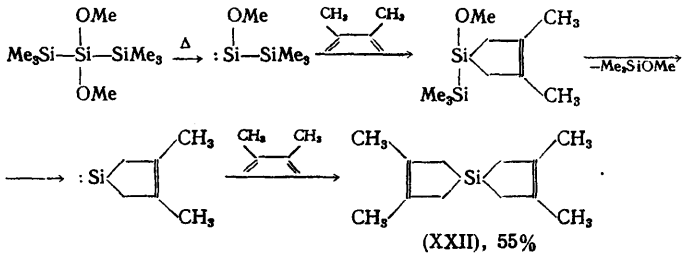


The formation of spiro compound (XXI) on copyrolysis of 2-cyclopropyl-2-methoxyhexamethyltrisilane with an excess of 2,3-dimethyl-1,3-butadiene was explained by the occurrence of a complex silylene–silene–silylene rearrangement including the formation of silacyclobutanylidene.[55]



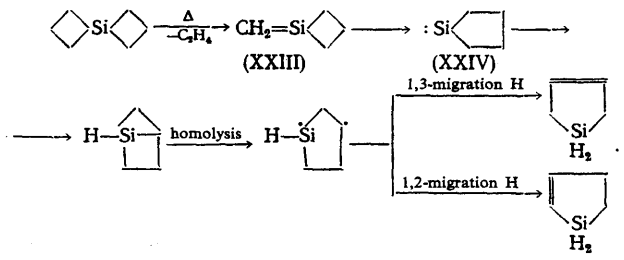
(XXI), 13%

Pyrolysis of 2,2-dimethoxyhexamethyltrisilane (450 °C, nitrogen stream) may be considered a convenient method of generating 3,4-dimethyl-1-silacyclopent-3-en-1-ylidene. Conducting the reaction in the presence of the trapping agent 1,3-dimethyl-1,3-butadiene leads to the formation of spiro compound (XXII).[56]

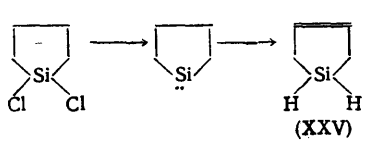


(XXII), 55%

Interesting results were obtained when studying the vacuum thermal decomposition of 3,3-silaspirocycloheptane.[57–59] It was assumed that the first stage of this process was the formation of silene (XXIII) which underwent rearrangement into silylene (XXIV) and subsequent intramolecular conversion as a result of which 1-silacyclopent-2-ene or 1-silacyclopent-3-ene were formed.

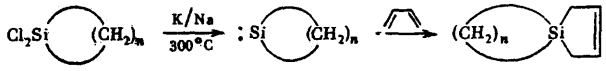


A gas phase method of generating silacycloalkanylidenes by reaction of dichlorosilacycloalkanes with alkali metal vapour (K/Na, 280–300 °C, 10^{-1} to 1.0 Torr) has been described,[60,61] for example:



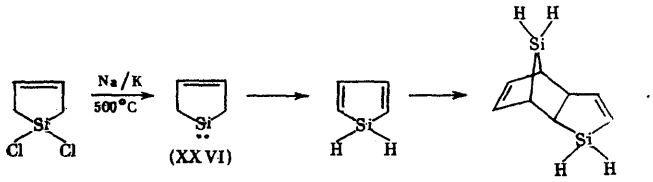
(XXV)

The formation of (XXV) is explained by intramolecular insertion of the initially formed unstable silacyclopentanylidene into the β C–H bond and subsequent conversion of the bicyclic intermediate. The cyclic silylenes obtained by dehalogenation are able to participate in [1 + 4] cycloaddition reaction with dienes such as 1,3-butadiene.

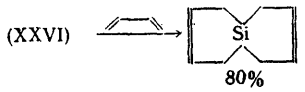


$n = 3 - 5$

The availability of the initial reactants makes the dehalogenation of organochlorosilanes by K/Na vapour a convenient method of generating cyclic silylenes and synthesising various spirane compounds with a central silicon atom.[62] For example reaction of 1,1-dichloro-1-silacyclopent-3-ene (500 °C, atmospheric pressure, argon atmosphere) with an excess of sodium or potassium leads to the formation of 1-silacyclopent-3-en-1-ylidene (XXVI).



The formation of (XXVI) was proved by trapping it with 1,3-butadiene.



80%

Investigation of the gas phase reactions of silylenes is developing intensively at the present time. In this project the thermal method must be considered as one of the most promising and hopeful, the wide use of which will lead to the discovery of both still unknown properties of silylenes and of sources for their generation.

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Cyclic mono- and diphosphazenes

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ABSTRACT. Methods of synthesis of 5- and 6-membered heterocyclanes with one or two endocyclic P=N bonds (cyclomono- and cyclodi-phosphazenes) have been considered. Types of reaction common to acyclic analogues and specific types of reaction have been separated. The change of electronic structure and geometry of the P=N bond on changing from linear to cyclic phosphazenes are clearly displayed in the special features of their chemical behaviour.

The bibliography has 247 references.

Contents

I. Introduction 538
II. Preparative methods 539
III. Special features of structure and reactivity 547

I. Introduction

The beginning of the seventies was a period of explosive development in investigations on phosphocyclanes in the chemistry of organophosphorus compounds.[1] This phenomenon also applies to heterocyclic compounds with an endocyclic P=N bond (cyclomono- and cyclodiphosphazenes). Acyclic phosphazenes were described for the first time by Staudinger in 1919,[2] however their systematic study began in 1950 with the work of Kirsanov and collaborators.[3–5] The first syntheses of six-membered cyclomono- and cyclodiphosphazenes appeared in the next decade,[5,6] as did those of five-membered analogues with dicoordinated[7] and tetracoordinated phosphorus atoms.[8,9]

The intensive investigations on organic cyclophosphazenes undertaken since the beginning of the seventies are reflected in a series of reviews published mainly in the foreign press.[10–14] Certain problems of the chemistry of these compounds have been touched upon in part.[15,16]

Interest in this area was caused by the special features of the structure and numerous chemical conversions of phosphacyclanes with a P=N bond, revealing broad vistas for the synthesis of various classes of *P,N*-containing compounds available for practical use.

A significant contribution has been made by Soviet investigators in the development of organic cyclophosphazene chemistry as is evident from an analysis of the literature.[6,10,11,14–16] There has been no correlation of these achievements in the domestic literature to date. Studies on heterocyclanes with one or two endocyclic P=N bonds are included in the present review. The cyclotriphosphazenes, having their own fairly complete literature converage,[17] have not been considered by us.

In contrast to acyclic compounds with a P=N bond, the nomenclature of which has an arbitrary character to a significant extent,[5,6,10,14] the naming of the corresponding cyclic organophosphorus compounds (OPC) is more uniform and corresponds to contemporary IUPAC rules.

This system will mainly be used in the present review. However it is convenient to use 'phosphazene' nomenclature, which has been widely adopted for some time, for linear and cyclic analogues as a general class of compounds with a P=N bond.[17] This nomenclature will be used for the general naming of the extensive series of compounds with a P=N bond.

The chemistry of heterocyclanes with a P=N bond is constructed on the basis of the experimental and theoretical developments of the acyclic phosphazenes. Consequently the synthetic methods for acycylic analogues are the basis for many means of obtaining cyclophosphazenes. Five of the basic reactions used for obtaining acyclic phosphazenes may be noted.[5]

The Staudinger reaction[2] comprises the reaction of organic azides with derivatives of tricoordinated phosphorus.

$$R_3P+R'N_3\rightarrow R_3P{=}NR'. \quad (1)$$

The reaction of dihalophosphoranes with compounds containing a primary amino group (the phosphazo reaction)[3–5]

$$R_3PX_2+R'NH_2\rightarrow R_3P{=}NR'. \quad (2)$$

The reaction of derivatives of tricoordinated phosphorus with compounds containing an amino group with two labile bonds (oxidation imination)[5,18]

$$R_3P + R'N\begin{matrix}X\\ \diagup\\ \diagdown\\ Y\end{matrix} \rightarrow R_3P{=}NR'. \quad (3)$$

An elimination reaction for compounds with a P–N bond[19–21]

$$R_3P\!-\!N\begin{matrix}R'\\ \diagdown\\ \diagup\\ Y\end{matrix} \rightarrow R_3P{=}NR'. \quad (4)$$
$$\quad\quad\quad

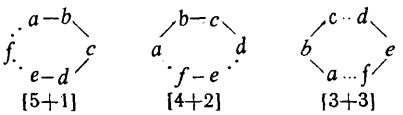
II. Preparative methods

1. Cyclocondensation reactions

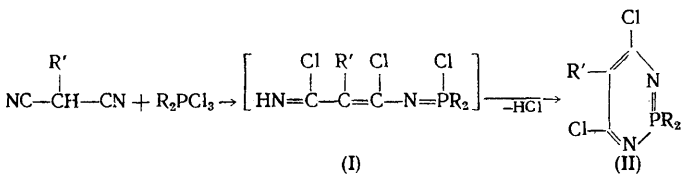
(a) Synthesis of hetero-1,2σ^4-azaphosphorines

The investigations of the Kiev school in conjunction with those of Kirsanov[6] and of Schmidpeter and colleagues[30] have made an important contribution to the development of the synthesis of six-membered cyclophosazenes. The reaction of nitrogen- and phosphorus-containing reactants by the phosphazo reaction with a subsequent cyclocondensation stage was a characteristic of all the proposed methods.

The synthesis of six-membered cyclophosphazenes may be formally represented as a number of elements participating in ring formation by [5 + 1]-,. [4 + 2]- and [3 + 3]-cyclocondensation reaction schemes.



One of the first representatives of the organic cyclophosphazenes, viz. 1,3,2-diazaphosphorine (II), was obtained by the interaction of malonic acid dinitrile with phosphorus pentachloride.[6]

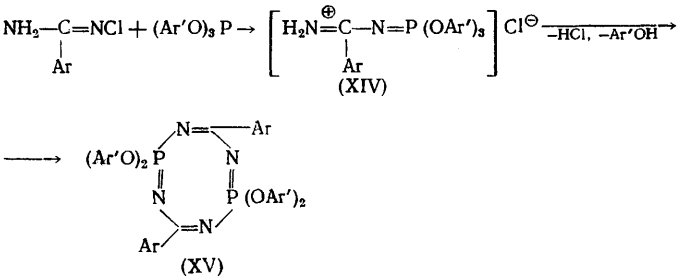


The authors suggested that the formation of a linear phosphazene (I) precedes the concluding stage. Study of the structure and routes of formation of diazaphosphorine (II) by the application of quantum chemical calculation methods has been carried out.[31]

Variants of the [5 + 1] scheme are the reaction of phosphorus pentachloride and certain trichlorophosphoranes with 1-amino-2-cyanoethylenes, *N*-cyanoamidines[6] and acetylurea[32] (Table 1, examples 1a, 1b, 2, 3a). Depending on the structure of the amino-containing reactant 1,3,2- (II) and 1,3,4-diazaphosphorines (III) or 1,3,5,4-triazaphosphorines (IV) were obtained. For [3 + 3] type cyclocondensations *P*-trichloro-*N*-dichloroalkylphosphazenes (VII)[6] and certain *N*-phosphorylated phosphazenes (IX), (X)[33–40] were reacted with nitriles, amidines and their salts. The structure of the resulting phosphorines (II), (IV), and (V) containing one or two P=N bonds was determined by the choice of phosphorus-containing reactant (Table 1, examples 1c, 3b, 4a, b). Triazamono- (IV) and triazadiphosphorines (V) were also obtained by a [4 + 2]-cyclocondensation of linear phosphazenes (VIII) and (XI) (Table 1, examples, 3c, 4c).[42]

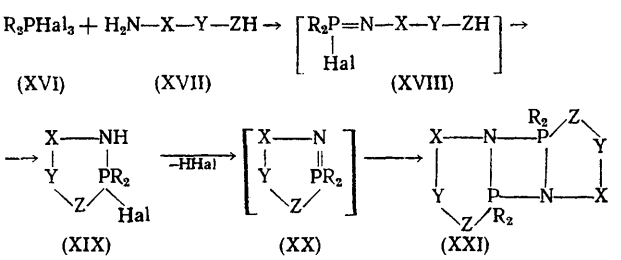
The multistage process of interacting *P*-trichloro-*N*-dichloroalkylphosphazene (VII) with ammonium chloride was carried out through the intermediate formation of alkylidenediphosphazene salts (XII) with isolation of triazadiphosphorine (V) [33,43,44] or a mixture of it with triazaphosphorine (IV) [6] (Table 1, example 4d). The synthesis of thioanalogues (VI) of triazadiphosphorines by a [5 + 1] scheme has been described.[45–50]

It is interesting to note the [4 + 4]-cyclocondensation reaction of hydrochloride salts of *P*-triaryloxy-*N*-iminoarylphosphazenes (XIV) as a rare example of the formation of 1,3,5,7,2,6-tetra-azadiphosphorine (XV).[51]



b) Synthesis of hetero-1,2σ^4-azaphospholes

Many methods of obtaining five-membered cyclophosphazenes are based on the interaction of halophosphoranes (XVI) with amino-containing compounds (XVII).



It is possible to represent the process by a single scheme, the initial stage of which is the formation of a linear phosphazene (XVIII). The latter undergoes intramolecular cyclisation into azaphospholine (XIX) with a pentacoordinated phosphorus atom. Further conversion of phosphacyclanes (XIX) occurs with elimination of hydrogen halide and the formation of 1,2σ^4-azaphospholes (XX) or their dimers (XXI).

The type of azaphosphole ring is determined mainly by the amino-component of the reaction for which oxalic acid diamides,[52] 2-aminoalkyl nitriles,[53] 4,5-diaminopyrimidines,[54] amidrazone hydrochlorides,[55,56] 1,2-aminophenols[57–60] and hydrazides of carboxylic[61–63] and thiocarboxylic acids[64] have been studied. The reaction of numerous reactants with phosphorus pentachloride or trichlorophosphoranes leads to the formation of 1,3,2σ^4-diaza- (XXII), (XXIII), 1,2,3,4σ^4-triaza- (XXIV), (XXV), and also isomer (XXVI), 4,5-benzo-1,3,2σ^4-oxaza- (XXVII), and 1,3,4,2σ^4-oxadiaza- (XXVIII) phospholes (Table 2).

In the majority of cases hetero-1,2σ^4-azaphospholes are unstable in the monomeric forms, they rapidly dimerise at the moment of formation. Exceptions are certain representatives of triazaphospholes (XXIV) and spirobis(triazaphosphole) (XXV). The latter is formed from triazaphosphole (XXIV) with an excess of amidrazone hydrochloride (XXIX).[65] 4,5-Pyrimidino-1,3,2-diazaphosphole (XXIII), characterised as the monomer,[54] seemingly exists in the dimeric form.

The problem of the stability of the monomeric and dimeric forms of hetero-1,2,-azaphospholes and the reason which causes a mixture of them in equilibrium has been discussed in several papers by Schmidpeter[53–57,64] and in detail in a review.[14] These problems will be considered in the present review only within the limits necessary for the characterisation of the chemical behaviour of the azaphospholes.

Table 1. Hetero-1,2σ^4-azaphosphorines by cyclocondensation reactions.

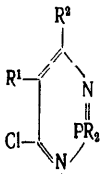
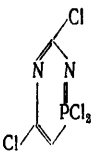
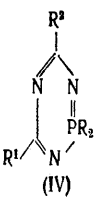
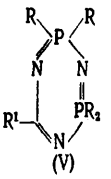
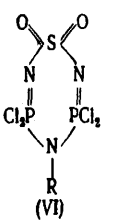
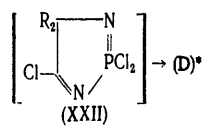
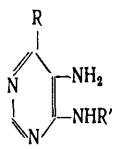
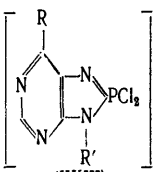
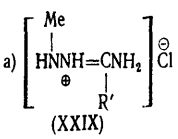
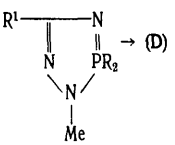
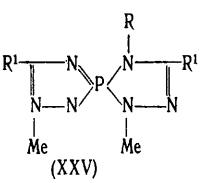
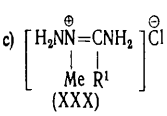
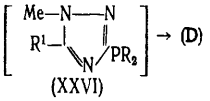
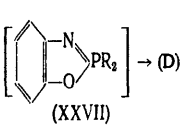
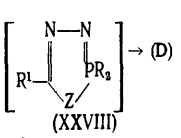
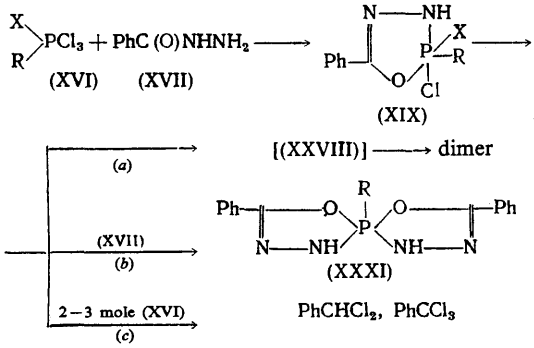
No.	Reactants		Reaction type	Azaphosphorine	^{31}P NMR, δ ppm	Refs.
	amino component	phosphorus component				
1	a) $R^1C(NH_2)=CCN$	R_2PCl_3	[5+1]	 (II)		[6]
	b) $NC-CH(R^1)-CN$	R_2PCl_3	[5+1]			
	c) R^1CH_2CN	$R^2CCl_2N=PCl_3$ (VII)	[3+3]			
2	$MeCNHCNH_2$ (O, O)	PCl_5	[5+1]	 (III)	53.0	[32]
3	a) $R^1C(NH_2)=NCN$	R_2PCl_3	[5+1]			
	b) $R^1C(NH_2)=NH.HCl$	(VII)	[3+3]	 (IV)	57.0 (R=Cl, N=PCl_3, R^1=R^2=Cl); 26.4 (R^1=H, R^2=NMe_2)	[6, 40—42]
	c) PhNHCH=NPh	$Me_2NC(NH_2)=NP(Ph)_2=NH$ (VIII)	[4+2]			
	d) $NH_2OH.HCl$	(VII)	[4+2]			
4	a) $R^1C(NH_2)=NH\cdot HCl$	$[R_2P(Cl)-N=PR_2(Cl)]^{\oplus}Cl^{\ominus}$ (IX)	[3+3]	 (V)	14.4 (R=Ph, R^1=H); 27.1 (R=Me, R^1=H); 36.0 (R=Cl, R^1=NMe_2); 40—43 (R=Ph, R^1=Ph, Cl)	[33—39, 43, 44]
	b) $R_FC(NH_2)=NH$	$Cl_2P(Ph)-N=PCl_2(Ph)$ (X)	[3+3]			
	c) PhNHCH=NPh	$R_2P(Cl)=N-P(NH_2)(Ph)=NH$ (XI)	[4+2]			
	d) NH_4Cl	$[RC(=\overset{\oplus}{N}PCl_3)(N=PCl_3)]\overset{\ominus}{X}$ (XII)	[5+1]	(IV)+(V)		[6]
5	a) $MeNH_2$	$(Cl_2P=N)_2SO_2$ (XIII)	[5+1]	 (VI)		[45—50]
	b) $(Me_3Si)_2NH$	(XIII)	[5+1]			

Table 2. Hetero-1,2σ^4-azaphospholes by cyclocondensation reactions.

No.	Reactants		Azaphospholes and their dimers	^{31}P NMR, δ ppm	Refs.
	amino component	phosphorus component			
1	a) NH_2CCNH_2 (O, O)	PCl_5	 → (D)* (XXII)	−48.0 (D)	[52—54]
	b) $NH_2C(R_2)CN$	PCl_5			
	c) 	PCl_5	 (XXIII)	—	[49]
2	a)  (XXIX)	R_2PCl_3	 → (D) (XXIV)	47.5—64.0 (M) **	[55, 56]
	b) (XXIX)	(XXIV)	 (XXV)	50.0 (M) (R^1=Ph, R=Me)	[65]
	c)  (XXX)	R_2PCl_3	 → (D) (XXVI)	−63.0 (D) (R^1=Cl)	[55, 56]
3	a) $C_6H_4(NH_2)(OH)$-1,2	R_2PCl_3	 → (D) (XXVII)	−43.0 — −48.0 (D)	[57—60, 68, 71]
	b) »	$RP(NEt_2)_2$			
	c) $C_6H_4(OH)(N_3)$-1,2	Et_2PCl			
4	a) R^1CNHNH_2 (Z)	R_2PCl_3	 → (D) (XXVIII)	−31.0 — −53.0 (D) (Z=O)	[61—64, 67]
	b) »	R_2PCl (Z)		−24.0 — −42.0 (D) (Z=S)	

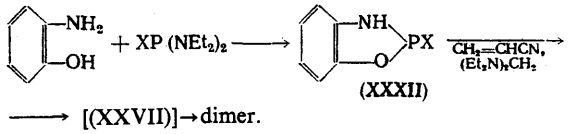
*D — dimer; **M — monomer.

The interaction of carboxylic acid hydrazides with halophosphoranes was historically the first and has been studied in most detail. The final result of the reaction depends mainly on the ratio of the initial reactants. At an equimolar ratio the process proceeds in accordance with the presented overall scheme and leads to dimers of 1,3,4,2σ^4-oxadiazaphospholes (XXVIII) (route a).[61,62] Hydrazides of thiocarboxylic acids reacted similarly at a 1 : 1 ratio.[64] At a two- and three-fold excess of phosphorus pentachloride decomposition of the intermediate oxadiazaphospholine (XIX) occurs (route c),[66] and in the case of a two-fold excess of hydrazide (XVII) spirodi(oxadiazaphospholines) (XXXI) were isolated.[63]



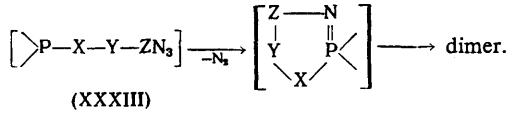
The acid chlorides of P(IV) acids or their thio analogues[61–64,67] were also used in reactions with carboxylic acid hydrazides (XVII). The latter were reacted at a ratio 1 : 1 and the former 1 : 3. In both cases dimers of 1,3,4,2σ^4-oxadiazaphospholes (XXVIII) were isolated as in the reactions with phosphoranes.[67]

The original method of synthesis of hetero-1,2,σ^4-azaphospholes was proposed in studies.[68–71] The authors used the high lability of the proton on the endocyclic nitrogen atom of 4,5-benzo-1,3,2-oxazaphospholanes (XXXII). As a result reaction was effected with acrylonitrile[68,70] and bisdiethylaminomethane[71] with the formation of 4,5-benzo-1,3,2-oxazaphospholes (XXVII), existing in the dimeric form.

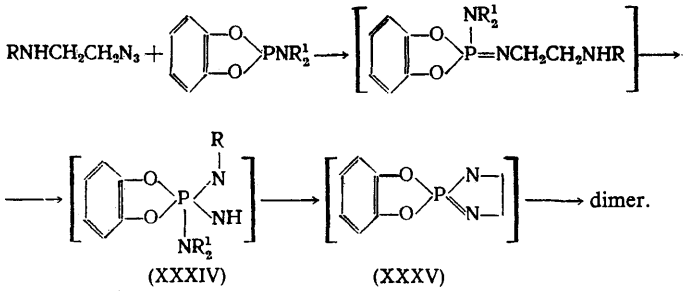


Analogous dimers of 4,5-benzo-1,3,2-oxazaphospholes (R = X = Ph) were formed from 4,5-benzo-2-methoxy-1,3,2σ^5-oxazaphospholanes by removing methanol thermally.[72] The course of the reaction through the unstable form (XXVII) was shown by reaction with aldehydes.

Intramolecular cyclocondensation of the Staudinger reaction type has also been studied with the aim of synthesising hetero-1,2-azaphospholes. In this scheme reaction was carried out between 2-hydroxyphenyl azide and diethylchlorophosphine[57,58] (Table 2, example 3c) and between 2-azidoalcohols and 1,2,4,3σ^2-triazaphospholes.[73] In both cases the 2-azidoaryl or 2-azidoalkyl derivatives of P(III) acids of the (XXXIII) type formed in the first step were subject to intramolecular cyclisation with separation of nitrogen.

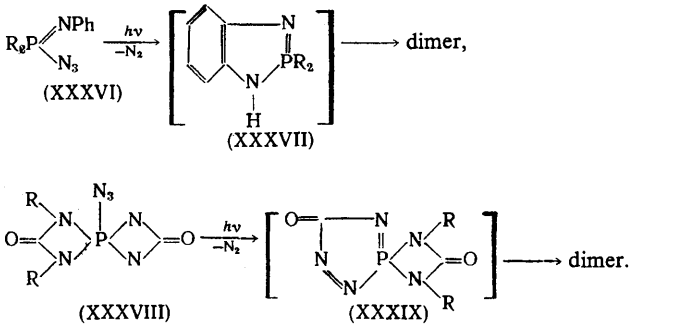


On interacting *N*-(2-azidoethyl)alkylamines with cyclic phosphites the first step was a Staudinger reaction completed by intramolecular cycloaddition and the formation of spirophosphoranes (XXXIV).[74]



The reaction led to the isolation of dimers of 1,3,2σ^4-diazaphospholines (XXXV). One of the alternative routes of forming them, proposed by the authors, may be the elimination of amine from a molecule of spirophosphorane (XXXIV).

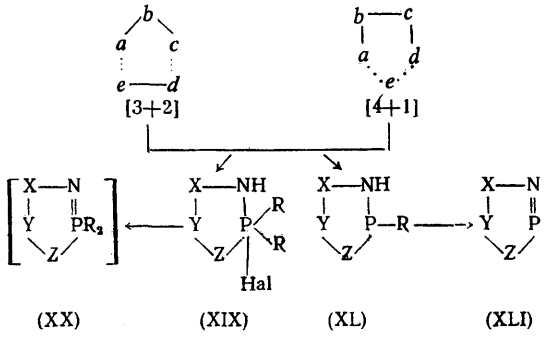
Azides of P(IV) (XXXVI) and P(V) (XXXVIII) derivatives may also be starting materials for obtaining dimers of hetero-1,2σ^4-azaphospholes (XXXVII) and (XXXIX). Photolytic decomposition of the azides was effected with simultaneous intramolecular cyclisation in the first case at the *ortho* position of the phenyl group and in the second at the nitrogen of the diazaphosphetidine ring.[12]



c) Synthesis of hetero-1,2σ^2-azaphospholes

The cyclocondensation reaction involving compounds of tricoordinated phosphorus is a source of many five-membered cyclophosphazenes with the coordinated of phosphorus equal to two. The first information on cyclophosphazenes with a low phosphorus coordination was published in 1963,[7] however the purpose directed synthesis of hetero-1,2σ^2-azaphospholes began to be intensively developed only after the work of Charbonnel and Barrans.[75]

When developing the analogy between the syntheses of hetero-1,2σ^4- and 1,2σ^2-azaphospholes it should be noted that the precursors of the desired products in both processes are unstable intermediates of type (XIX) or (XL). They may be formed by [3 + 2]- or [4 + 1]-cyclocondensation schemes. Conversion of the intermediates into 1,2σ^4- (XX) or 1,2σ^2-azaphospholes (XLI) respectively occurs with loss of one of the exocyclic substituents at phosphorus and by reduction of the phosphorus coordination to 4 or 2.



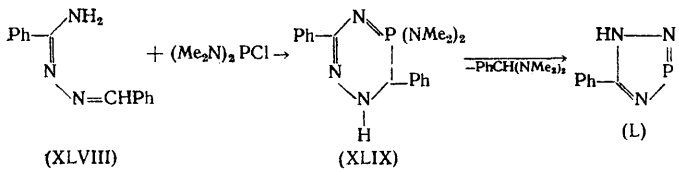
(XX) (XIX) (XL) (XLI)

The types of hetero-1,2σ^2-azaphospholes (XLIII)–(XLVII), (LI) and (LVII) synthesised on the basis of cyclocondensation reactions are shown in Table 3. As is seen from Tables 2 and 3 the synthesis of hetero-1,2σ^4-azaphospholes proceeds mainly by a [4 + 1] scheme but a [3 + 2]-cyclocondensation scheme also occurs for hetero-1,2σ^2-azaphospholes. In addition to these, intramolecular cyclocondensation (Table 3, example 1b)[13] and 'reductive elimination' (example 1c)[34] reactions have been developed for 1,3,2σ^2-diazaphosphole (XLIII).

The first representative of the azaphospholes, viz. 4,5-benzo-1,3,2σ^2-azaphosphole (XLV),[7] as shown by later investigations,[76] exists in crystals in the form of a tetramer.

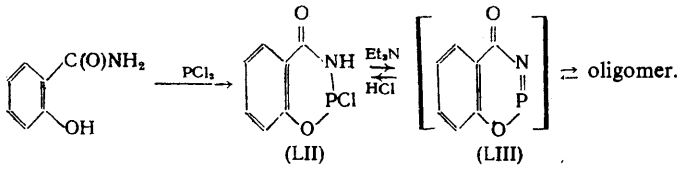
1,2,4,3σ^2-Triazaphospholes (XLVI) and (XLVII) were obtained by reacting methylimidates with chlorophosphines.[75] This reaction takes place through a stage of forming phosphinoimidates[77] (Table 3, example 2a). The latter react with monosubstituted hydrazines with the separation of two regioisomers α-(XLVI) and β-(XLVII) possessing different thermal stabilities. Only one α-isomeric form (XLVI) was isolated from the reaction of amidrazone hydrochlorides with tris(dimethylamino)phosphines[77,78] (example 2b).

An unusual method of obtaining *N*-protonated 1,2,4,3σ^2-triazaphospholes (L) has been described.[79] It is based on the reaction of tetramethyldiaminochlorophosphine with azine (XLVIII), the resulting 1,2,5,4σ^4-triazaphosphorine (XLIX) is converted into triazaphosphole (L) with separation of aminal.



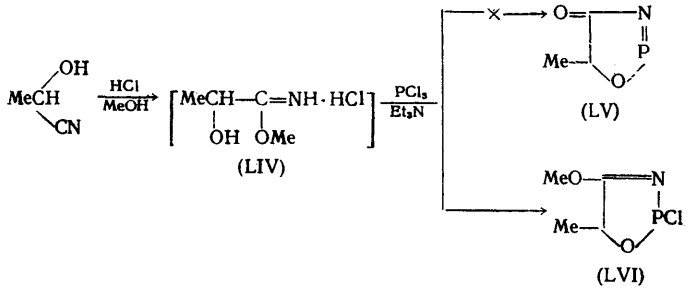
(XLVIII) (XLIX) (L)

In contrast to the stable monomeric diaza- and triazaphospholes described above (Table 3) 1,3,2σ^2-oxazaphosphole (LI) was obtained as the tetramer (Table 3, example 3).[84] Similarly reaction of salicylic acid amide with phosphorus trichloride is terminated by the formation of an oligomer of 4-keto-5,6-benzo-1,3,2σ^2-oxazaphosphorine (LIII).[85] On treatment with hydrogen chloride the oligomer is converted once again into oxazaphosphorine (LII) evidently through the monomeric form (LIII).



(LII) (LIII)

Unsuccessful attempts to obtain 4-keto-1,3,2σ^2-oxazaphosphole (LV) also point to the low thermodynamic stability of the endocyclic O–P=N system.[86] 1,3,2σ^3-Oxazaphospholine (LVI) was isolated in place of the desired product from the reaction of imidate hydrochloride (LIV) and phosphorus trichloride.



(LIV) (LV) (LVI)

The reaction of tetrachloromethylenediphosphine with hydrazine led to the formation of 1,2,3,5σ^2-diazadiphosphole (LVII) which is the first representative of a diphospha-1,3-diene system (Table 3, example 4).[87]

2. Cycloaddition reactions

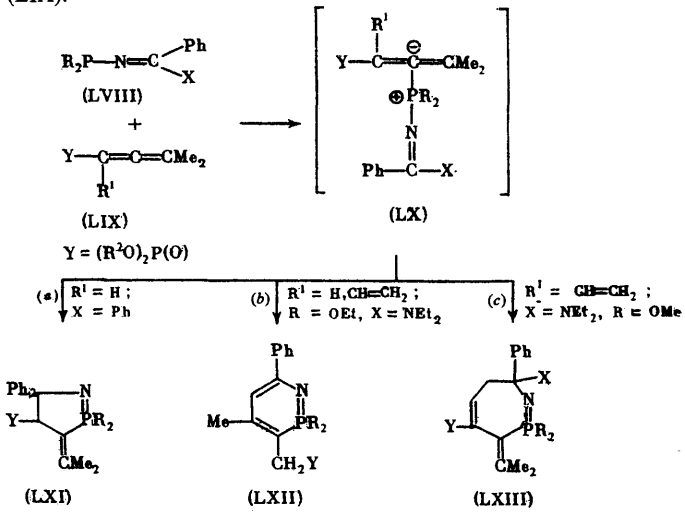
Cycloaddition reactions have a significant role in the chemistry of heterocyclic compounds. Development of these reactions applied to the P=N bond systems has opened new prospects for the synthesis of five- and six-membered cyclophosphazenes. The use of 'non-classical' 1,3-dipoles =P–X=Y (or =P–X≡Y) for the construction of phosphorus-containing rings has been considered.[9,88] Experimentally these ideas were confirmed by the synthesis of [3 + 3]-cyclic adducts with a P=C bond,[16,89] and also of [3 + 2]-cyclic adducts[8,9,90] and [3 + 3]-cyclic adducts[91,92] with P=N bonds.

Cycloaddition reactions involving heteroatomic 1,3-dipoles have been considered in reviews,[15,16] the few examples of obtaining cyclophosphazenes up to that time are included there. Of the approximately 35 types of cyclophosphazenes known today more than half were synthesised by cycloaddition reactions.

a) Synthesis of hetero-1,2σ^4-azaphosphorines

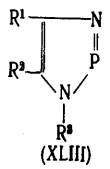
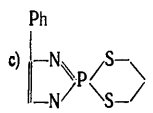
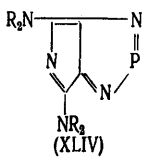
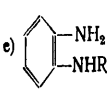
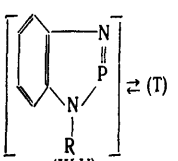
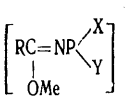
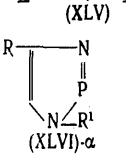
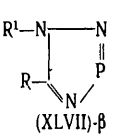
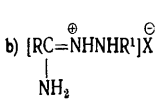
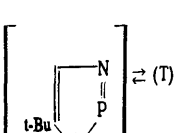
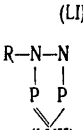
Both [3 + 3]- and [4 + 2]-cycloaddition reactions are used in methods of synthesising the indicated cyclophosphazenes (Table 4).

1,2-Azaphosphorines (LXII) were isolated from the reaction of methyleneaminophosphines (LVIII) and allenylphosphonates (LIX).[93–96]



(LVIII) (LIX) (LX) (LXI) (LXII) (LXIII)

Table 3. Hetero-1,2σ^2-azaphospholes by cyclocondensation reactions.

No.	Reactants		Reaction type	Azaphosphole monomer→tetramer*	^{31}P NMR, δ ppm	Refs.
	amino component	phosphorus component				
1	a) NCC=CCN NH_2 NH_2 (XLII)	PCl_3	[4+1]		255 [(R¹=R²=(N≡C)]	[80—83]
	b) $MeNP(NMe_2)_2$ CH_2CN	—	intramaolecular cycloaddition	 (XLIII)		[13]
	c) 	—	reductive elimination			[34]
	d) R_2NH + 2 (XLII)	PCl_3	[4+1]	 (XLIV)	299—301	[78, 81—83]
	e) 	$P(NMe_2)_3$, $P(OPh)_3$	[3+2]	 ⇄ (T) (XLV)	228—236; 81—89 (T)	[7, 76]
2	a) R^1NHNH_2		[3+2]	 (XLVI)-α	251—256	[75, 77]
				 (XLVII)-β	257	[77, 78]
	b) 	$(Me_2N)_3P$	[4+1]	(XLVI)	—	
3	t-$BuCCH_2NH_2$ O	PCl_3	[4+1]	 ⇄ (T) (LI)	269.5	[84]
4	$RNHNH_2$	$CH_2(PCl_2)_2$	[3+2]	 (LVII)	—	[87]

*T — tetramer.

Two possible reaction routes have been established for α-unsubstituted ($R^1 = H$) allenylphosphonates, viz. a [3 + 2]-cycloaddition (route a) and a [3 + 3]-cycloaddition (route b).[93,94] The presence of a readily removable group X on the methylene carbon of the methylenaminophosphine (LVIII) is very important for the success of the reaction route.

In the case of α-vinylallenylphosphonate [$R^1 = (CH=CH_2)$] two dipolarophilic centres capable of participating in cycloaddition are competing.[95] The reaction proceeds by routes (b) or (c) depending on the nature of the alkoxy substituents at the phosphorus of methylenaminophosphorine (LVIII). Data from kinetic measurements and quantum chemical calculations were in agreement with the proposed two-stage reaction mechanism through the initial formation of the dipolar ion (LX).[96]

As mentioned above the first [3 + 3]-cycloaddition reaction of phosphorus-nitrogen-containing 1,3-dipoles was carried out for the reaction of diphenylisocyanatophosphine (LXV) with nitrilimines (LXVI) (Table 4, example 2).[91,92] The activity of the phosphorus-containing dipoles in reactions with such classical 1,3-dipoles fell according to the following series.[97,98]

$$ArPNCO > (ArO)_2PNCO > R_2PN{=}C\begin{matrix}R^1\\R^2\end{matrix}$$

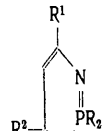
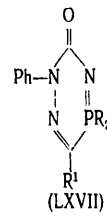
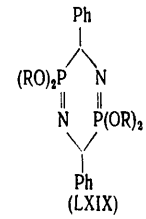
In contrast to methylenaminophosphines (LVIII), which have two alkyl or aryl substituents at the methylene carbon, benzylidene-aminophosphine (LXVIII) possessed increased activity.[99] At the moment of preparation it rapidly dimerised by [3 + 3]-cycloaddition with the formation of 1,4,3,6-diazadiphosphorine (LXIX) (Table 4, example 3).

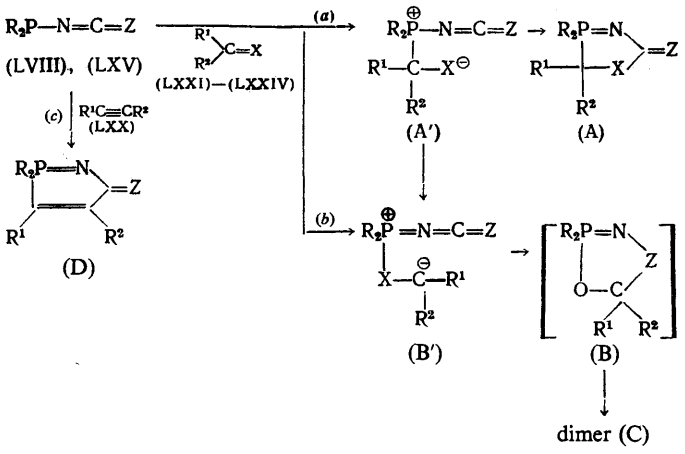
The Diels-Alder reaction has also been investigated with a view to synthesising 1,2-azaphosphorines.[100] The linear phosphazene (LXIV), obtained by reaction of phosphines with alkene azides, was used as diene in this reaction. The [4 + 2]-cycloadduct from the reaction of diene (LXIV) with alkynes was not isolated but was converted into the more stable 1,2-azaphosphorine (LXII) (Table 4, example 1b).

b) Synthesis of hetero-1,2σ^4-azaphospholes and azaphospholines

Like the syntheses of 1,2-azaphosphorines described above, the [3 + 2]-cycloaddition reaction leading to the formation of five-membered cyclophosphazenes has been studied in detail mainly for two phosphorus-nitrogen-containing 1,3-dipoles, viz. methylen-aminophosphines (LVIII) ($Z = R^1, R^2$) and isocyanatophosphines (LXV) ($Z = O, S$) (Tables 5, 6). Reaction of these 1,3-dipoles proceeded with the formation of cyclic adducts of types (A)–(D) depending on the nature of the dipolarophile.

Table 4. Hetero-1,2σ^4-azaphosphorines by cycloaddition reactions.

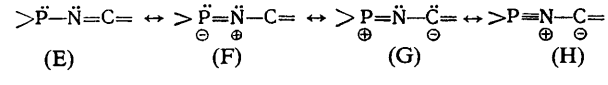
No.	Dipole (diene)	Dipolarophile (dienophile)	Reaction type	Azaphosphorine	^{31}P NMR, δ ppm	Refs.
1	a) $R_2PN{=}C(R^1)X$ (LVIII)	$(R^4O)_2P(O)R^5{-}C{=}CR^2_2$ (LIX)	[3+3]	 (LXII)	39–55	[93–95]
	b) $[R_3P{=}NC{=}CH_2]R^1$ (LXIV)	$R^2C{\equiv}CR^3$	[4+2]			[100]
2	R_2PNCO (LXV)	$R^1C{=}NNPh$ (LXVI)	[3+3]	 (LXVII)	—	[91, 92, 97]
3	—	$[PhCH{=}NP(OR)_2]$ (LXVIII)	[3+3]	 (LXIX)	40.7; 38.3 ($R=OCH_2CH_2O$) 42.1; 40.7 ($R=OC_6H_4O$-1,2)	[99]



The [3 + 2]-cycloaddition of phosphorus-containing 1,3-dipoles to dipolarophiles (LXXI)–(LXXIV) was characterised in the majority of studies as a two-stage process, beginning with nucleophilic attack of the phosphorus atom on the electrophilic centre of the dipole (route a).[11,16,97] After formation of the bipolar ion (A′) conversion proceeds further to cyclic adduct by direct cyclisation to azaphospholine (A) or through first isomerisation into ion (B′) and subsequent cyclisation to the unstable azaphospholine (B) which dimerises.[11] An alternative route (b) was proposed for the reaction of methylenaminophosphines with 4-nitrobenzaldehyde.[101] It is quite probable that the interaction of substituted alkynes (LXX) (route c) may proceed via a concerted cycloaddition mechanism; however, there are no kinetic data to date on this type of reaction. It should be noted that not all the studied combinations of 1,3-dipoles and dipolarophiles lead to the isolation of cyclophosphazenes (A) or (B). In many cases the formation of cyclic adducts is accompanied by their further conversion. They will be considered in more detail when discussing the chemical properties of the five-membered cyclophosphazenes.

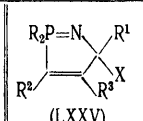
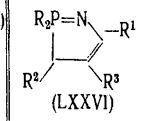
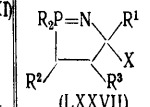
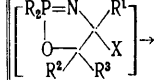
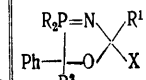
Various structures for the synthesised heterophosphacyclanes (LXXV)–(LXXXIV) were achieved by varying the dipolarophile component of the reaction.

As is seen from Tables 5 and 6 a wide range of dipolarophiles of the classes of unsaturated and carbonyl compounds (LXX)–(LXXIV) was investigated in the reactions with phosphorus- and nitrogen-containing 1,3-dipoles. Analysis of the experimental data showed that a decisive role in determining the course of the processes and also the formation of regioisomers is played by the initial step comprising nucleophilic attack by the phosphorus atom of the 1,3-dipole on the electrophilic centre of the dipolarophile. This was confirmed by the observation that cycloaddition reactions are accelerated with an increase in the nucleophilicity of the phosphorus atom.[96,97,128] and also the order of addition to substituted alkenes,[9,102,104,119] aldehydes[121–128] and other dipolarophiles.[129–131] Consequently structures (E) and (F) of the resonance structures of 1,3-dipoles make the major contribution.

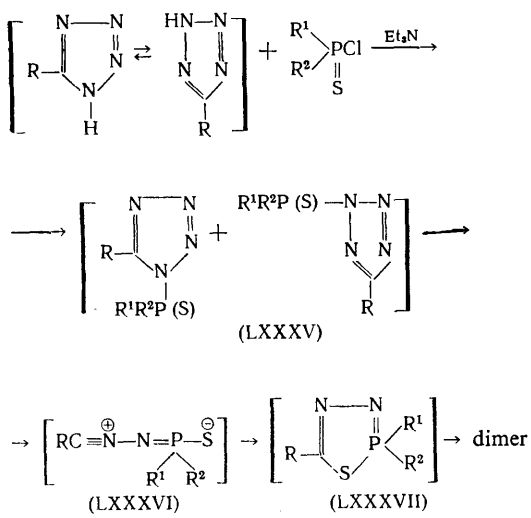


In this case the order of addition of certain carbonyl compounds requires particular consideration. The reaction of these compounds proceeds with the formation of monomers of type (A) or the regioisomeric cyclic adducts (B), which exist in the form of dimers (C). The different order of addition is explained by isomerisation of the bipolar ion (A′) into ion (B′) (see general scheme.[11] However in certain cases with an insignificant difference in structure of dipolarophile (examples 4, 5 in Table 5, examples 4c, 5a in Table 6, etc.) the process is directed either towards 1,4,3-oxazaphospholines (LXXIX), (LXXXIII), or towards 1,3,2-oxazaphospholines (LXXVIII), (LXXXIV) or their dimers. There is still no complete explanation for this.

Table 5. Hetero-1,2σ^4-azaphospholes and 1,2σ^4-azaphospholines by cycloaddition reactions of methylenaminophosphines (LVIII).

No.	Dipolarophile	Azaphospholes, azaphospholines	^{31}P NMR, δ ppm	Refs.
1	$R^2C{\equiv}CR^3$ (LXX) a) $R^2{=}R^3{=}COOMe$ b) $R^2{=}H$, $R^3{=}COOMe$ c) $R^2{=}Me$, $R^3{=}COOMe$ d) $R^2{=}Ar$, $R^3{=}COOMe$	 (LXXV)	47.4 ($R{=}R^1{=}X{=}Ph$, $R^2{=}R^3{=}COOMe$)	[9, 102–104]
2	$R^2CH{=}CHR^3$ (LXXI) a) $R^2{=}Me$, $R^3{=}COOR$ b) $R^2{=}Me$, $R^3{=}CN$ c) $R^2{=}Ph$, $R^3{=}COOR$ d) $R^2{=}Ph$, $R^3{=}C(O)R$ e) $R^2{=}H$, $R^3{=}CN$	 (LXXVI)	57.9 ($R{=}Ph$, $R^1{=}OEt$, $R^2{=}H$, $R^3{=}CN$)	[105]
3	$R^2CH{=}CR^3R^4$ (LXXII) a) $R^2{=}R^4{=}H$, $R^3{=}COOMe$ b) $R^2{=}R^4{=}H$, $R^3{=}C(O)Me$ c) $R^2{=}R^4{=}H$, $R^3{=}CN$ d) $R^2{=}(R^5O)_2P(O)$; R^3, $R^4{=}(=CR^6_2)$	 (LXXVII)	48–75	[9, 94, 102–104]
4	 (LXXVIII) a) $R^2{=}H$, $R^3{=}C_6H_4NO_2$-4 b) $R^2{=}Me$, $R^3{=}C(O)Me$ c) $R^2{=}Ph$, $R^3{=}CN$ d) $R^2{=}Ph$, $R^3{=}CH_2C(O)Me$		46.0 ($R{=}OMe$, $R^1{=}Ph$, $X{=}OEt$, $R^2{=}CN$, $R^3{=}Ph$) −58.0 (D) ($R^1{=}X{=}Ph$, $R^2{=}H$, $R^3{=}C_6H_4NO_2$-4)	[101, 107–110]
5	 a) $R^2{=}COOEt$, $R^3{=}Ph$ b) $R^2{=}P(O)(OEt)_2$, $R^3{=}Ph$	 (LXXIX)	—	[106]

Of other cycloaddition reactions it is possible to cite the method of obtaining dimers of 1,3,4,2-thiadiazaphospholes (LXXXVII) from thiophosphorylated tetrazoles (LXXXV).[64] Pyrolysis of the latter leads to ring opening and the formation of a linear phosphazene (LXXXVI) which undergoes rapid intramolecular cycloaddition and dimerisation.

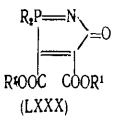
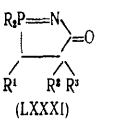
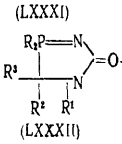
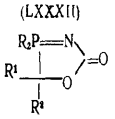
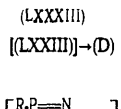


(LXXXV)

(LXXXVI) (LXXXVII)

The $1,2\sigma^2$-azaphospholes, which retain their endocyclic P=N bond during several transformations, may be starting materials for obtaining hetero-$1,2\sigma^4$-azaphospholes. [4 + 1]-Cycloaddition reactions of α-dicarbonyl compounds[133] and esters of azodicarboxylic acids[134] to $1,2\sigma^2$-azaphospholes are known. A series of spirocyclic phosphazenes was obtained in this way both in the dimeric[134] and in the monomeric form.[133]

Table 6. Hetero-$1,2\sigma^4$-azaphospholines by cycloaddition reactions of isocyanatophosphines (LXV).

No.	Dipolarophile	Azaphospholine	^{31}P NMR, δ ppm	Refs.
1	$R^1OOCC{\equiv}CCOOR^1$ (LXX)	 (LXXX)	–	[90, 98, 111]
2	$R^1CH{=}CR^2R^3$ (LXXI) a) R^1=H, R^2=Br, R^3=CN b) R^1=H, R^2=Br, R^3=COOMe c) R^1=Me, R^2=CN, R^3=COOEt	 (LXXXI)	24–30	[112, 113]
3	a) $CCl_3CH{=}NR^1$ (LXXIII) b) R^1NCO (LXXIV)	 (LXXXII)	62.0 (R=OMe, R^3=H, R^2=CCl_3; −70–−80 (D) [R^2, R^3=(=O)]	[129–132]
4	R^1(R²)C=O (LXXII) a) R^1=H, R^2=CCl_3 b) R^1=H, R^2=XC_6H_4	 (LXXXIII)	71–76 (R=OAlk); 59–62 (R=Ph)	[8,121–128]
	c) R^1=Ph, R^2=CN d) R^1=H, R^2=CCl_3	[(LXXIII)]→(D)	−40–−60 (D) (R=$OAlk_F$)	[114–116]
5	R^1(R²)C=O (LXXII) a) R^1=Ph, R^2=C(O)Ph b) R^1=R^2=CF_3 c) R^1=CF_3, R^2=(iso-PrO)$_2$P(O)	 (LXXXIV)	−54.0 (D) (R=OMe, R^1=R^2=Ph)	[117–120]

Several other reactions of $1,2\sigma^2$-azaphospholes and also the conversions of $1,2\sigma^4$-azaphosphole dimers, described in part III of the present review, may be considered as sources for obtaining five-membered cyclophosphazenes.

Only one type of four-membered cyclophosphazene is known as yet, viz. diazadiphosphetine (XC), obtained by photolysis of diisopropylphosphine azide (LXXXVIII).[12,135,136] Reaction occurred through a reactive intermediate (LXXXIX) which was dimerised already at −42 °C.

$$[(\text{iso-Pr})_2\text{N}]_2\text{PN}_3 \xrightarrow{h\nu} \{[(\text{iso-Pr})_2\text{N}]_2\text{P}{\equiv}\text{N}\} \rightarrow \{[(\text{iso-Pr})_2\text{N}]_2\text{P}{=}\text{N}\}_n$$

(LXXXVIII) (LXXXIX) n = 2 (XC); 3 (XCI).

The molecular structure of dimer (XC) was demonstrated by X-ray structural analysis.[135] Trimerisation of the intermediate (LXXXIX) was observed in addition to dimerisation. The formation of diazadiphosphetine (XC) (42% yield) was preferred in comparison with triazatriphosphorine (XCI) (3% yield).

III. Special features of structure and reactivity

Much attention has been paid in recent years to the clarification of the special features of the electronic structure of the P=N bond. The data obtained enable an understanding of the peculiarities of the structure and chemical behaviour of phosphazenes when compared with their heteroanalogues. It is known that in their properties phosphazenes occupy an intermediate position in the series of compounds with isoelectronic groups P=X (X = C, N, O, S).[28,29] They have a higher bond order than phosphorus ylids which was confirmed by their higher ionisation potentials[138] and by the P=N bond lengths.[137]

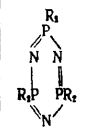
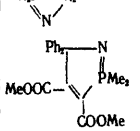
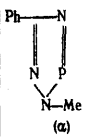
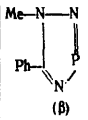
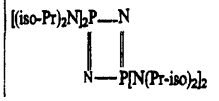
A model molecule $Me_3P{=}NH$ was assigned to the π-type from the results of HOMO quantum chemical calculations and this was confirmed experimentally by photoelectron spectroscopic data.[138] At the same time the P=N bond is significantly more polarised than the phosphoryl or thiophosphoryl bonds.[139–141]

The special features found for the P=N bond, particularly the double bond character with a significant contribution of polar structure and its ready polarisability, mainly predetermine the chemical behavior of acyclic and cyclic phosphazenes. However a change in the electronic properties of the P=N group and the geometry of its components caused by the presence of a ring introduce specific features into their chemical behaviour. A theoretical analysis of the structure of acyclic and five-membered cyclic phosphazenes with a tetracoordinated phosphorus atom has been carried out.[14] In comparison with acyclic analogues[137] transition into a cyclic phosphazene is accompanied by a significant reduction in the endocyclic angles at phosphorus and nitrogen (Table 7). As a result of the angular strain in the five-membered phosphazene ring there is an increase in the *p*-character of the valence orbitals of the phosphorus atom and in the lengths of the endocyclic bonds with neighbouring atoms. The changes in structure and electronic properties are displayed in an increase in the electrophilicity of the phosphorus atom, an increase in the polarity of the P=N bond,[14] and a tendency to transition of the five-membered cyclophosphazenes into phosphacyclanes with pentacoordinated phosphorus. In the latter the gain in energy is explained by the small structural changes required for conversion of σ^4- into σ^5-phosphacyclanes.[57,142]

Conclusions on the specific features of the P=N bond in five-membered rings were confirmed by the accumulated experimental

material both on some of their physical properties and on their chemical behaviour. The value of the screening constant of the phosphorus atom nucleus was an indicator in this respect. A very broad range for the chemical shifts of the ^{31}P nucleus (δ_P + 40 to −98 p.p.m.) was characteristic of acyclic phosphazenes with tetracoordinated phosphorus. Their values were in a complex non-additive dependence on the nature of the substituents at phosphorus and nitrogen.[143–147]

Table 7. Structural parameters of the endocyclic Y−P=N−X fragment of cyclophosphazenes.

No.	Compound	Bond length P=N, Å	Angle P=N−X, deg	Angle Y−P=N, deg	Refs.
1		1.54–1.60	120–148	115–126	[17]
2		1.579	111.5	98.6	[142]
3	 (α)	1.616	108.9	92.4	[154]
4	 (β)	1.627; 1.637	106.6	97.0; 97.0	[155] [156]
5		1.651	85.0	95.0	[135]

The screening constants for five-membered cyclophosphazenes lie within much closer limits and depend to a lesser degree on the environment of the phosphorus atom. For example, for the most studied 1,2σ^4-azaphospholes and 1,2σ^4-azaphospholines the resonance signals were observed in the region δ_P 76 to 48 p.p.m. (Tables 5, 6) and for 1,3,2σ^4-diaza- and 1,2,4,3σ^4-triazaphospholes were in the region 83 to 61 p.p.m.[30] It is characteristic that this region of appearance in low field is comparable with that for acyclic phosphazenes with a polarised P=N bond.[28,137,141,143–146]

The narrow range of values for the ^{31}P nuclear screening constants in the hetero-1,2σ^4-azaphospholes and -azaphospholines may serve as a diagnostic tool when establishing the structure of these cyclanes. The exceptions were the five-membered spirocyclophosphazenes in which the chemical shift of the ^{31}P nucleus was displaced towards higher field (50 to 15 p.p.m.).[60,73,133]

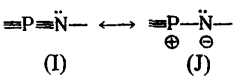
The ^{31}P nuclear resonance signals for hetero-1,2σ^4-azaphosphorines were observed within the limits δ_P 14 to 57 p.p.m. (Tables 1, 4). The breadth of the limits and the displacement towards higher field indicate the less polar character of the P=N bond in six-membered cyclophosphazenes. This conclusion was confirmed by the chemical behaviour of the azaphosphorines, distinguished by high stability. The changes mentioned in the character of the phosphazene bond were the result of a reduction of the angular stress in the six-membered ring and its partial aromaticity due to the delocalisation of π-electrons in the endocyclic P=N−X system.[6,17,34] The degree of delocalisation of π-electron density and the conductance of the electronic influence of the P=N−X fragment of diaza- and triazaphosphorines has been studied[148,150] using the ^{35}Cl NMR method and quantum chemical calculations.

In contrast to hetero-1,2σ^4-azaphospholes the corresponding phosphacyclanes with a dicoordinated phosphorus atom possess a lower inclination to react at the P=N bond.[13,77,151–153] The increased stability of the 1,2σ^2-azaphospholes is explained by the presence of aromatic character in these heterocycles. The molecular structure of 1,2σ^2-azaphospholes demonstrates the closeness of the configuration of the valence *p*-orbitals of the phosphorus atom to an ideal orthogonal configuration (Table 7).[154–158]

The resonance region of the dicoordinated phosphorus atom nucleus was specific (Table 3). It is easily possible to distinguish hetero-1,2σ^2-azaphospholes from the corresponding compounds of tetracoordinated phosphorus by ^{31}P NMR spectral data. Important characteristics were obtained by NMR spectral methods (^{31}P, ^1H, ^{13}C) and were used for the identification of the structures of these cyclanes.[13] A correlation of ^{15}N and ^{31}P nuclear chemical shifts has been carried out.[159]

1. Interaction with nucleophilic and electrophilic reagents

The nucleophilic character of the phosphazene bond is explained by the contribution of both the resonance structure (I) and structure (J). In addition it is known that compounds with a P=N bond also possess electrophilic properties in the display of which a significant role is played by the contribution of structure (J).[137,138,141]

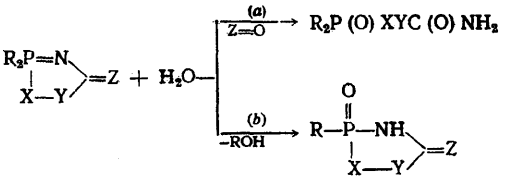


(I) (J)

The stability of acyclic phosphazenes $R_3P{=}NR^1$ towards the action of nucleophilic reagents depends on the substitutents R and R_1 and varies within wide limits.[5,28,29,137]

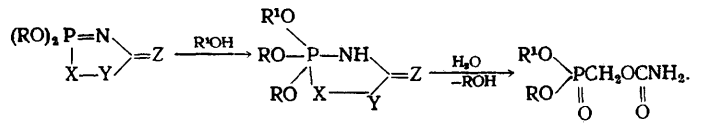
Regarding the polar character of the P=N bond the cyclophosphazenes are more stable to the action of water, alcohols, amines and other reagents with labile protons.

Hetero-1,2σ^4-azaphospholes and -azaphospholines are readily, partially at the time of isolation, subject to hydrolysis. This reaction occurs in the majority of cases with opening of the ring at the P=N bond (route *a*), however there are examples of ring retention (route *b*).



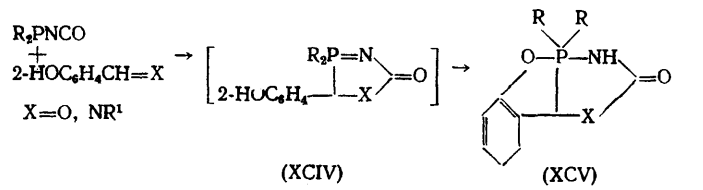
1,2-Azaphospholes,[90,111] azaphospholines,[93–95] and 1,3,4-oxazaphospholines[122–128] react by route (*a*). A wide range of *C*-phosphorylated carbamates has been obtained based on this and investigated.[121,125,160–163] A course of hydrolysis by route (*b*) has been recorded for 1,2,4,3-triazaphospholes,[56] phosphorylated 1,2-azaphospholes[94] and 1,3,4-diazaphospholines.[164]

The interaction of five-membered cyclophosphazenes with alcohols is readily effected. Relatively stable addition products (XCII) were successfully obtained for 1,3,2σ^4- [101] and 1,3,4-σ^4-oxazaphospholines.[165] These were rapidly hydrolysed with the isolation of carbamates (XCIII) with mixed substituents on phosphorus.[166]



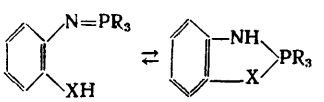
Z=O, (R^2, R^3) (XCII) (XCIII)

The thermodynamically more stable cyclic phosphoranes (XCV) were obtained on interacting isocyanatophosphines with ortho-hydroxysubstituted aromatic aldehydes [167,168] and amines,[169] and also with fluorinated acetylacetone.[170]



(XCIV) (XCV)

The intermediate formation of cyclic adducts (XCIV) was not recorded either during the reaction process or in solutions of phosphabicyclane (XCV).[168] In contrast to this it was possible to observe the tautomeric equilibrium of phosphazene and phosphorane structures in a series of linear *N*-2-hydroxy(amino)phenyl-phosphazenes (XCVI).[171–173]

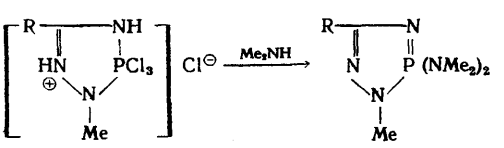


(XCVI)

This fact, and also the examples given above of reactions with water and alcohols demonstrate the low thermodynamic stability of five-membered rings with a P=N bond, being subject to facile conversion into phosphacyclanes with a pentacoordinated phosphorus atom.

The reactions of dimeric five-membered cyclophosphazenes with water and alcohols seemingly occur through the monomer formation stage. The presence of the monomer even in infinitesimally small concentration enables rapid flow of the process because of its high reactivity. The hydrolysis of 1,3,2σ^4-diazaphosphole dimers [52,53] and the reaction of 1,2,4,3σ^4-triazaphospholes with *p*-cresol [56] proceed in this way.

Five-membered cyclophosphazenes are more stable towards the action of amines. Treatment of 1,2,4,3σ^4-triazaphospholine salts (XCVII) or its dimer with a secondary amine leads only to replacement of chlorine atoms at phosphorus and isolation of free triazaphosphole (XXIV).[56] Products of addition at the P=N bond were not observed.

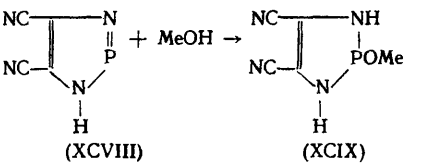


(XCVII) (XXIV)

The low reactivity towards amines made it possible to develop a synthesis of monomeric spirocyclophosphazenes (XXV) based on the reaction of triazaphosphole dimers (XXIV) with *N*-methyl-benzamidrazone hydrochloride (XXIX) [65] (Table 2, example 2b).

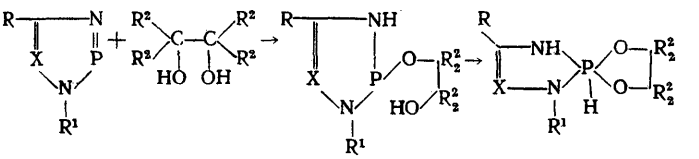
In contrast to the dimers of triazaphospholes (XXIV) the dimers of oxa- and thiadiazaphospholes (XXVIII) react with diethylamine in the dimeric form. Replacement of chlorine at phosphorus was readily effected in this way.[64]

The reactivity of hetero-1,2σ^4-azaphospholes was reduced in comparison with their analogues with a tetracoordinated phosphorus atom and depended on the degree of aromaticity of the azaphosphole ring. 1-Methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (XLVII) (β-isomer), possessing little aromaticity, did not react with alcohols or amines, but 2-methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (XLVI) (α-isomer) adds alcohols, primary and secondary amines at the P=N bond.[77] However such weak nucleophiles as carboxylic acids, aromatic amines or β-naphthol did not react with the α-isomer. Alcohol added more readily to 1,3,2σ^2-diazaphosphole (XCVIII) with the formation of the corresponding 1,3,2-diaza-phospholine (XCIX).[81]



(XCVIII) (XCIX)

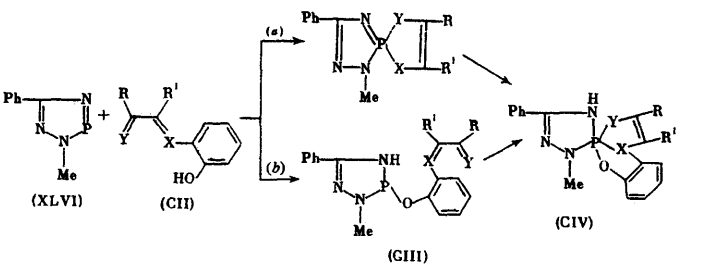
The reaction of 1,2-diols with 1,2,4σ^2-triaza- (XLVI) [77] and 1,3,2σ^2-diazaphosphole (XLIII) [81] was accompanied by subsequent cyclisation at the tricoordinated phosphorus atom of intermediate (C) with the formation of spirophosphoranes (CI).



(XLIII), (XLVI) (C) (CI)

1,2-Aminoalcohols and 1,2-diamines reacted in a similar manner.

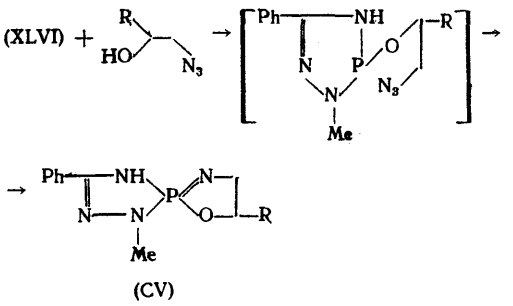
The reaction of 2-methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (XLVI) with phenols (CII) containing a diene grouping in the ortho position has been studied.[153]



(XLVI) (CII) (CIII) (CIV)

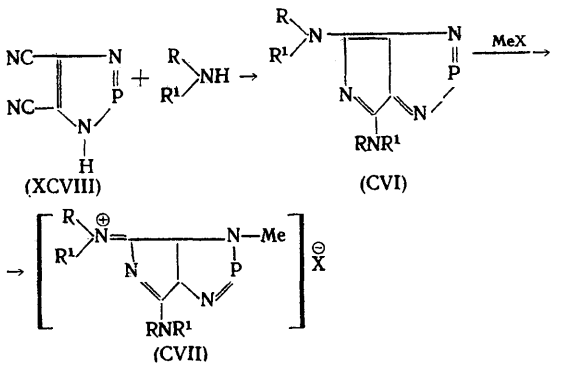
The authors claimed that of the two possible routes the process is effected by route (*b*) with the initial 1,2-addition of the hydroxyl group of reactant (CII) and subsequent intramolecular [4 + 1]-cycloaddition of the intermediate (CIII). The interaction of triazaphosphole (XLVI) with azido alcohols is assigned to the same type.[73] As in the reactions shown above the present process does not stop at the stage of addition of the P=N bond. Cyclisation is

further brought about by a reaction of the Staudinger type with the formation of a new spirocyclophosphazene (CV).



(CV)

Interesting results have been obtained on reacting 1,3,2σ^2-diazaphosphole (XCVIII) with secondary amines.[80–83] The presence of a diazaphosphole ring activated the nitrile group. The latter proved to be capable of adding amine with the formation of 4,5-pyrrolo-1,3,2σ^2-diazaphosphole (CVI). In this the (σ^2) P=N bond was retained.

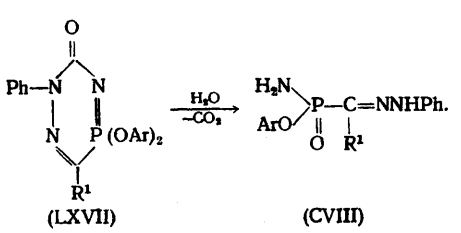


(XCVIII) (CVI) (CVII)

Alkylation of the product (CVI) with the formation of salt (CVII) was carried out on the diazaphosphole ring with retention of the phosphorus coordination.

The six-membered cyclophosphazenes occupy an intermediate position between the five-membered analogues and cyclotriphosphazenes in regard to the action of nucleophiles. Their reactivity is determined to a significant degree by the nature of the substituent at phosphorus. Thus 1,3,5,2,4-triazadiphosphorine (V) (Table 1, example 4) with methyl substituents at phosphorus dissolves readily in cold water without decomposition.[36,42] The corresponding chloro derivatives (V) are hydrolysed under these conditions, the authors claim, at one of the phosphazene bonds without ring scission,[34] but heating 2,2,4,4-tetraphenyl-1,3,5,2,4-triazadiphosphorine with water led to rupture of the ring.

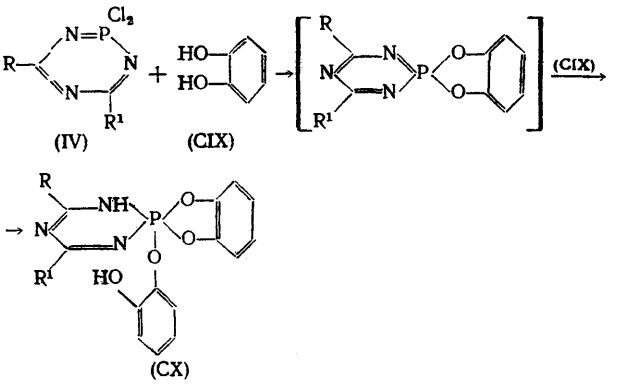
An unusual course for the reaction with water was found for 1,3-aryl-6-oxo-1,2,5,4-triazaphosphorine (LXVII) hydrolysis of which was accompanied by decarboxylation and led to the *C*-phosphorylated hydrazone (CVIII).[97]



(LXVII) (CVIII)

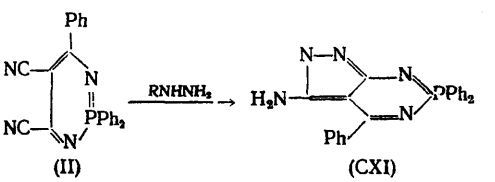
1,2-Azaphosphorines (LXII) (Table 4)[6,93] and eight-membered cyclophosphazenes (XV) [51] are hydrolysed at the P=N bond with retention of the ring.

The reaction of 2,2-dichloro-1,3,5,2-triazaphosphorines (IV) with diols in the presence of base occurs with substitution of chlorine and retention of the phosphazene bond in the ring.[174] However on using ortho-hydroquinones 1,2-addition at the P=N bond was observed in addition to substitution and spirophosphoranes (CX) were obtained.



(IV) (CIX) (CX)

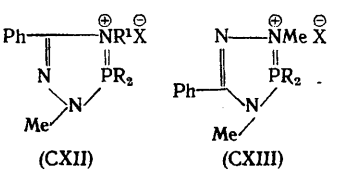
Chloro-substituted 1,3,2-diaza- (II) and 1,3,5,2-triazaphosphorines (IV) enter into exhaustive substitution reactions with aliphatic amines, phenoxides and alkoxides. The P=N bond is not affected by this. 4-Chloro-5-cyano derivatives of (II) react with *N*-substituted hydrazines with the formation of condensed heterocycles (CXI) without participation of the P=N bond.[6]



(II) (CXI)

In contrast to the acyclic phosphazenes[28,29,137,175–178] there are no systematic investigations on the basicity of the cyclophosphazenes which is seemingly connected with their low stability. Nonetheless examples have been described of the formation of cyclophosphazene salts in reaction with hydrogen chloride and with alkyl halides.

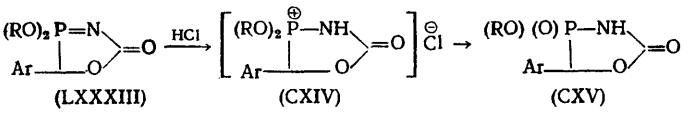
Salts of 1,2,4,3-triazaphospholes (CXII) and (CXIII) have been established by ^{31}P NMR. By removing hydrogen chloride, salt (CXII) (R^1 = H) is readily converted into the corresponding azaphosphole or its dimer.[56]



(CXII) (CXIII)

Alkylation of 1,2,4,3-triazaphospholes (XLVI) and (XLVII) has been carried out with the formation of salts of analogous structure. It was noted that azaphospholines (LXXVII) were more basic than 1,2-azaphospholes (LXXV) (Table 5) in reaction with hydrogen chloride.[179] 1,4,3-Oxazaphospholines (LXXXIII), with alkoxyl substitutents at phosphorus, were readily converted by hydrogen

chloride into oxazaphospholidines (CXV). The reaction evidently proceeds through the formation of phosphonium salt (CXIV).[180]



(LXXXIII) (CXIV) (CXV)

Similarly the monomeric product of addition of the P=N bond appeared on reaction of dimeric 1,3,2-oxazaphospholes (LXXVIII) (Table 5) with hydrogen chloride and was decomposed further with rupture of endocyclic bonds at phosphorus.[67]

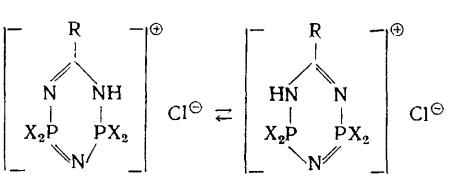
The basic properties of hetero-1,2σ^2-azaphospholes are weakly expressed because of the less polar character of the P=N bond. Thus 1,2,4,5σ^2-triazaphospholes possess such a low basicity that they are not protonated by acetic or trichloroacetic acids and do not give salts with methyl iodide.[77] 1,3,2σ^2-Diazaphospholes display acidic properties with strong bases. Their ammonium and potassium salts react with methyl iodide at the nitrogen atom neighbouring the P=N bond.[81–83] In all these conversions the coordination of phosphorus is retained equal to two.

Hydrogen chloride adds at the P=N bond of hetero-1,2σ^2-azaphospholes. This reaction is the reverse of the dehydrochlorination of 1,2σ^3-azaphospholidines which leads to the formation of azaphospholes with dicoordinated phosphorus.[56,77,81,83,85]

Bromination and chlorination of 1,2,4,3σ^2-triazaphospholes takes place with retention of the P=N bond and leads to the dimer of 1,2,4,3σ^4-triazaphospholes (XXVI) (Table 2).[55,56,77] The authors claim that the target products were the result of a more complex process than a 1,2-addition reaction at the (σ^2) P atom.[13]

Organomagnesium compounds react with 1,2,4,3σ^2-triazaphospholes (XLVI) at the P=N bond, electrophilic attack at the (σ^2) P atom is effected in this.[181]

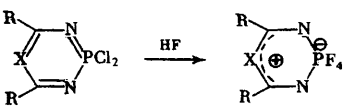
The basicity of hetero-1,2-azaphosphorines is determined by the nature of the substituent at phosphorus as in the reactions with nucleophiles described above. So 2,2,4,4-tetrachloro-1,3,5,2,4-triazaphosphorines (V) are not alkylated by alkyl halides.[33] Replacement of the chlorine atoms at phosphorus by aryl groups leads to a strengthening of the basic properties of the triazaphosphorines (V). In the case of the 2,2,4,4-tetraphenyl derivatives fairly stable hydrochloride salts (CXVI) were obtained, the structure of which has been investigated by NMR spectroscopy (^{31}P, ^{1}H).[34] It was shown that protonation of the nitrogen takes place at position 1 or 5 but the phosphorus atoms in cations (CXVI) are magnetically equivalent. This corresponds to the presence of degenerate tautomerism of both protonated forms.



(CXVI)

Salts (CXVI) were hydrolytically less stable than the free bases, they were readily hydrolysed or alcoholised with ring rupture between nitrogen and phosphorus at positions 1 and 2.[35]

1,3,2-Diaza- (II) and 1,3,5,2-triazaphosphorines (IV) add two molecules of hydrogen fluoride with simultaneous exchange of halogen at phosphorus. The final product was cyclic salt (CXVII) in the molecule of which the negative charge was localised at the (σ^6) P.[182]



(II), (IV) (CXVII)

X = CCl, CH, N

2. Cycloaddition reactions

Cycloaddition reactions have been best studied for five-membered cyclophosphazenes with a tetracoordinated phosphorus atom. This clearly marked trait of their chemical behaviour is caused by the polar character of the P=N bond and an inclination towards transition to the energetically more favourable cyclanes with a pentacoordinated phosphorus atom.

Dimerisation reactions are a characteristic of many types of hetero-1,2σ^4-azaphospholes and azaphospholines. The reasons influencing the position of the equilibrium between monomeric and dimeric forms have been fairly well studied to date.[14,55–58,64] Among azaphospholines and azaphospholes structures have been found for which the position of the equilibrium is shifted either towards the monomeric or the dimeric forms. If attention is paid only to the nature of the endocyclic atoms in the N=P–X fragment then the inclination towards dimerisation of five-membered cyclophosphazenes grows along the series X = C < N < O.[56,57] There are only a very few cyclophosphazenes with an endocyclic P–C bond existing in the dimeric form. 1,3,4σ^4-Oxazaphospholines (LXXXIII) with electron-accepting exocyclic substituents at phosphorus[114–116] and 2-oxo-1,3,4-diazaphospholines (LXXXII) (Table 6, examples 3b 4c, d)[129–131] belong to these.

The preferential existence of cyclanes with an N=P–C fragment in the monomeric form is explained by the transition to the dimer being disadvantaged by the high activation energy of the process. The increase in energy is linked with the need for such a configuration of the dimer when the five-membered ring is forced to occupy a diequatorial position due to the weak apicophilicity of carbon. The indicated transition is unfavoured especially in the presence of apicophilic exocyclic substitutents at phosphorus.[14]

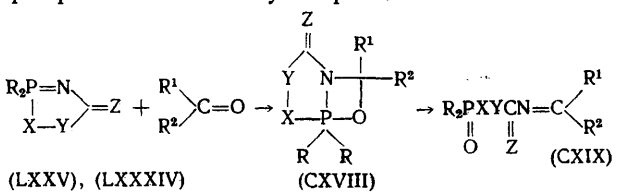
When the neighbouring atom X in the endocyclic N=P–X fragment is nitrogen the position of the monomer⟷dimer equilibrium depends on the fine balance of electronic and steric influences of the exocyclic substituents.[14] Representatives existing only in the form of monomers[56,65,133] or dimers[52,53,56,67,134] are found among this type of 1,3,2σ^4-diazaphospholes.

When an endocyclic N=P–O fragment is present the five-membered cyclophosphazenes exist in the crystal almost exclusively in the dimeric form.[57–60,68–70,73,107,108,110] There is only one example of the monomeric form for 1,3,2σ^4-oxazaphospholine (LXXXIV) in the solid state (Table 6, example 5c).[118]

The possibility of conversion into the monomeric form in solution has been proposed to clarify several chemical properties of the cyclophosphazene dimers. Such a conversion has been observed for dimers of 1,3,2-oxazaphospholines (LXXXIV) in solution.[68,73] The presence of the monomeric form in solution was confirmed experimentally in competing [2 + 2]-cycloaddition reactions.[56,67,72]

In addition to dimerisation five-membered cyclophosphazenes with a tetracoordinated phosphorus atom readily participate in [2 + 2]-cycloaddition reactions with several compounds with

multiple bonds. In contrast to acyclic phosphazenes[5] primary products of cycloaddition (CXVIII) with pentacoordinated phosphorus were isolated or established in the majority of reactions of cyclophosphazenes with carbonyl compounds.



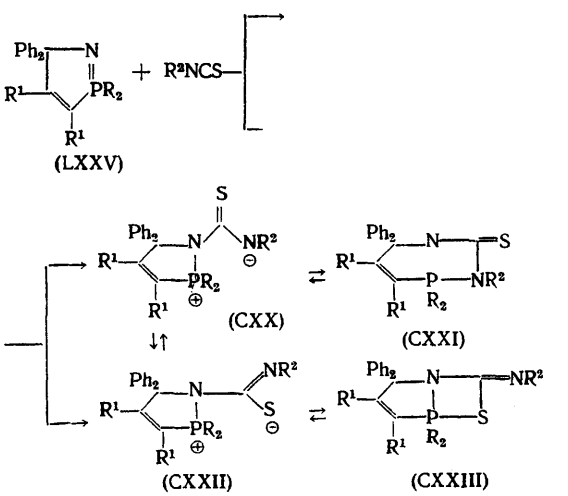
(LXXV), (LXXXIV) (CXVIII) (CXIX)

The interaction of 1,3,2σ^4-oxazaphospholine (LXXXIV) (Table 6, example 5b) with hexafluoroacetone has been described.[120] Stable bicyclic adducts (CXVIII) were successfully isolated and studied by X-ray analysis in reactions of 1,2-azaphospholes (LXXV) (Table 5, example 1c) with ketones.[142,183] On heating, bicyclanes (CXVIII) were converted into linear imines (CXIX).

The same, but less stable, bicyclic adducts of type (CXVIII) were obtained by reaction of 1,2-azaphospholes (LXXV) with chloroacetone.[184] The formation of intermediates (CXVIII) was not observed in analogous reactions with aldehydes, linear imines (CXIX) were isolated directly as final products.[101,183] However, on using chloral, bicyclanes (CXVIII) stable at low temperature were established spectrally.[180]

Dimers of 1,3,2σ^4-oxazaphospholes (LXXXIV) have been successfully introduced into competing [2 + 2]-cycloaddition reactions due to their partial dissociation in solution. A bicyclic adduct of type (CXVIII) was isolated on reaction with methyl isocyanate,[67] but an imine of type (CXIX) on reaction with ketones.[72] Similarly dimers of triazaphospholes (XXVI) (Table 2, example 2) reacted with phenyl isocyanate through the monomeric form with the formation of bicyclic adduct (CXVIII).[56]

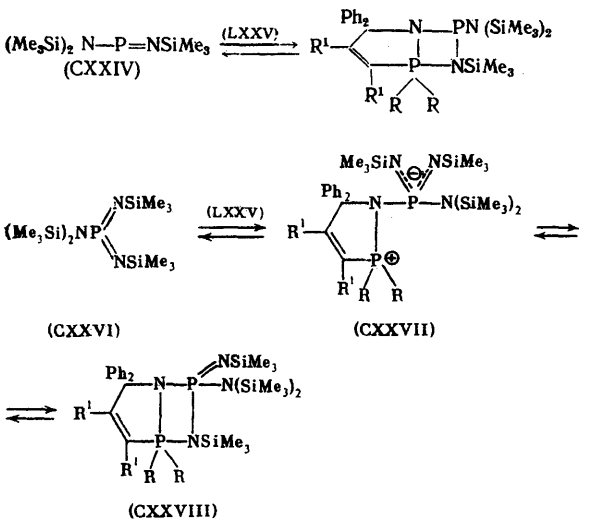
The [2 + 2]-cycloaddition of isothiocyanates to 1,2-azaphosphole (LXXV) occurred by two routes with the participation of both heteroatom double bonds.[185]



(LXXV) (CXX) (CXXI) (CXXII) (CXXIII)

The course of the process along one or the other route was determined by the substituent on the isothiocyanate group. Methyl isocyanate reacted with the C=N bond with the formation of a stable bicyclic adduct (CXXI). Isothiocyanates with more electron-accepting substituents [R^2 = $Ph_2P(S)$; PhC(O)] led to the product of cycloaddition at the C=S bond (CXXIII). When the dipolarophilic activity of the isothiocyanate double bonds [R^2 = $Me_2P(S)$; Me] was the same, reaction occurred simultaneously by the two routes. The composition of the resulting mixture of cyclic adducts depended on the nature of the solvent and on concentration. The latter fact, in the authors' opinion, indicates the presence of a labile equilibrium between the final cyclic adducts (CXXI) and (CXXIII), and their ionic forms (CXX) and (CXII). The presence of such an equilibrium was confirmed spectroscopically.

In addition to carbonyl compounds, linear $\sigma^2\lambda^3$-diazaphosphazene (CXXIV) and $\sigma^3\lambda^5$-triazaphosphazene (CXXVI) have also been used in cycloaddition reactions of 1,2σ^4-azaphospholes (LXXV).[186] Cyclic adducts (CXXV) and (CXXVIII) were found in solution in equilibrium with the starting materials, and in the case of triazaphosphazene (CXXVI) the bipolar ion (CXXVII) also participated in the equilibrium.

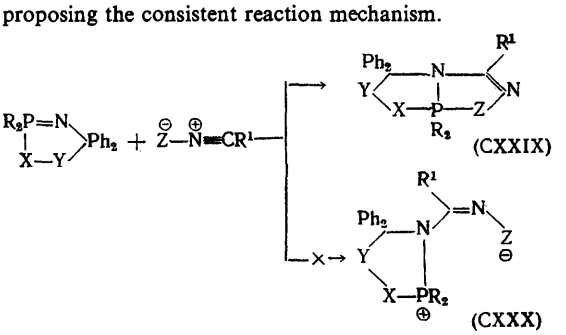


(CXXIV) (CXXVI) (CXXVII) (CXXVIII)

The spectrally observed formation of bipolar ion (CXXVII),[186] and also the possibility of transition of cyclic adducts through bipolar ions (CXXI)⇄(CXX)⇄(CXXII)⇄(CXXIII) [185] point in favour of a stepwise mechanism for the [2 + 2]-cycloaddition reaction of 1,2σ^4-azaphospholes.

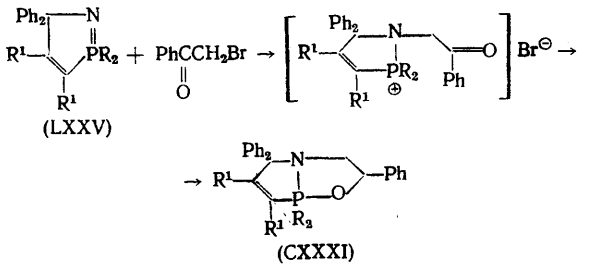
It should be mentioned that the reverse reaction, viz. dissociation into starting materials, is observed for many five-membered cyclophosphazenes and the products of their [2 + 2]-cycloaddition in solution.[123,126,179,183–186] In the majority of cases the process is reversible.

Hetero-1,2σ^4-azaphospholes and azaphospholines take part in [3 + 2]-cycloaddition reactions with such classical 1,3-dipoles as nitriloxide, nitrilimines and nitrones.[179] In all cases, except for 3,4-dihydroquinoline *N*-oxide, the formation of stable crystalline cycloaddition products (CXXIX) was recorded. Checking the reaction by ^{31}P NMR spectroscopy failed to detect the presence of bipolar ion (CXXX) as a possible intermediate which was a basis for proposing the consistent reaction mechanism.



(CXXIX) (CXXX)

In contrast to that given above the reaction of 1,2σ^4-azaphosphole (LXXV) with bromoacetophenone occurred through the stage of a phosphonium intermediate.[184]



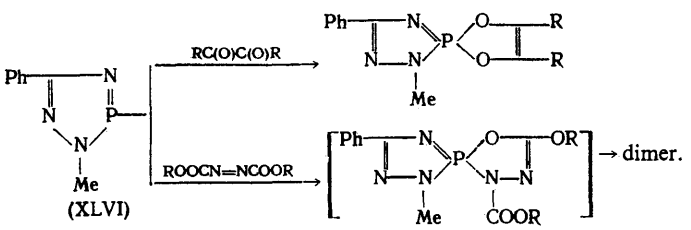
(LXXV) (CXXXI)

The formation of bicyclic adducts analogous to (CXXXI) was also observed in the reaction with styrene oxide. It is impossible to attribute reaction with the latter two reactants to the classical [3 + 2]-cycloaddition reaction.

1,2σ^2-Azaphospholes proved to be less inclined towards dimerisation and cycloaddition reactions due to the aromatic character of the azaphosphole ring and the lower polarity of the phosphazene bond.

Of the known types of hetero-1,2σ^2-azaphospholes (Table 3) 4,5-benzo-1,3,2σ^2-diazaphospholes (XLV) and 1,3,3,σ^2-oxazaphospholes (LI) exist in the form of tetramers, however they readily pass into the monomeric form in solution or on heating.[7,76,84]

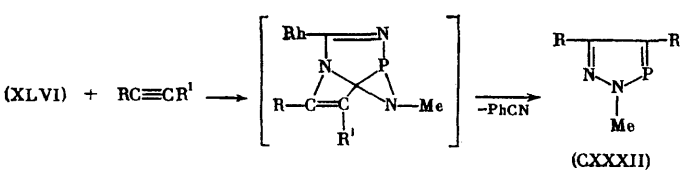
The reduced activity of 1,2,4,3σ^2-triazaphospholes (XLVI) was displayed in reactions with 1,2-diketones[133] and esters of azodicarboxylic acid[134] which reacted according to a [4 + 1] type of cycloaddition at the phosphorus atom without participation of the phosphazene bond.



(XLVI)

The reactions shown demonstrate the possibility of using 1,2,4,3σ^2-triazaphospholes for the synthesis of the corresponding spirocyclophosphazenes with a tetracoordinated phosphorus atom. However, 1-phenyl-1,2,3,5σ^2-diazadiphosphole (LVII) did not react with diacetyl by the reaction indicated.[87]

There are data on the participation of triazaphosphole (XLVI) as dienophile in a [4 + 2]-cycloaddition reaction with a substituted acetylene.[187] The authors claimed the intermediate formation of cyclic adducts the observation of which was unsuccessful. Diazaphospholes (CXXXII) with a (σ^2) P=C bond were isolated by elimination of nitrile.

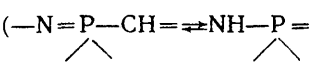


(CXXXII)

A similar reaction has also been described for 1,3,2σ^2-diazaphospholes (XLIII).[82]

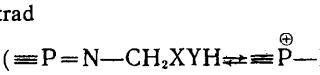
3. Rearrangements in the cyclophosphazene series

Several types of rearrangement and heterotropic conversion have been found for acyclic phosphazenes. Reversible and irreversible silylotropic rearrangements are known[188–193] as are prototropic tautomeric conversions in triad



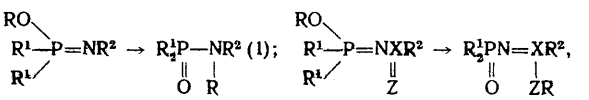
[194–197]

and tetrad



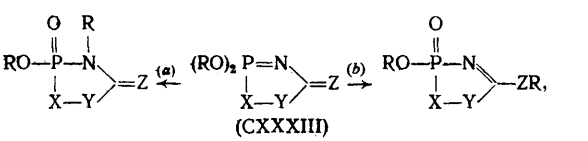
[198–200]

systems. The ring-chain tautomeric equilibrium in compounds with a P=N bond may also be assigned to the latter system.[171,172,200] The imide–amide (1) and imide–imide (2) rearrangements of acyclic phosphazenes have been considered in a review.[27]



X=C, P; Z=O, S.

Two reactions of the latter type in the cyclophosphazene series have been studied widely and systematically by Pudovik and Konovalova and their co-workers.[11,15] The subjects of the investigation, viz. hetero-1,2σ^4-azaphospholines (CXXXIII), were rearranged thermally without isolation by routes (*a*) or (*b*) in the majority of cases.[115,201–209]

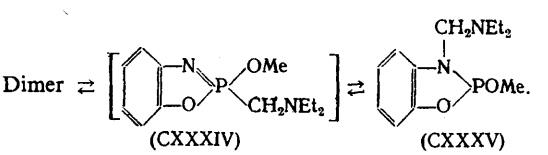


(CXXXIII)

Z=O, S, (R^1, R^2).

Frequently both processes occurred simultaneously,[210–212] although rearrangement by route (*b*) was more characteristic for thione derivatives of (CXXXIII).[213–215]

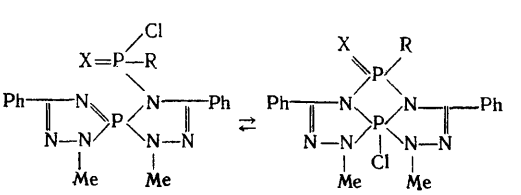
In contrast to compounds (CXXXIII) 4,5-benzo-1,3,2-oxazaphospholine (CXXXIV) underwent an imidophosphonate–amidophosphite rearrangement under distillation conditions.[70,71]



(CXXXIV) (CXXXV)

Oxazaphospholine (CXXXV) formed on distillation is slowly (60 days) transformed at room temperature once again into the dimer evidently through the monomeric form (CXXXIV).

A new type of chlorotropic ring–chain tautomerism has been described for *N*-substituted 3,3-spiro-di(1,2,4,3σ^4-triazaphospholes) (CXXXVI).[65]

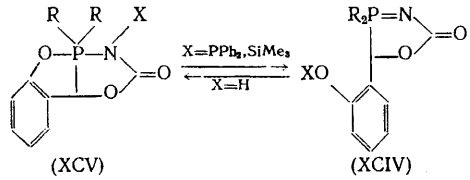


(CXXXVI) (CXXXVII)

X=O, unshared electron pair.

The position of the (CXXXVI)⇄(CXXXVII) equilibrium depends on the electron-accepting properties of the substituent at phosphorus. The equilibrium is completely displaced either to the left or to the right for the extreme members of the series R = Ph, Me_2N, PhO, Cl (X = unshared electron pair), Cl (X = O), an equal mixture of tautomers was observed for an average member.

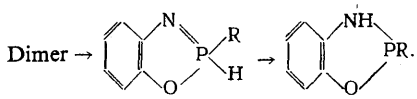
An irreversible phosphoro- and silylotropic transition (σ^5)→(σ^4) P was found in the triad system of oxazaphosphabicyclooctane (XCV).[169]



(XCV) (XCIV)

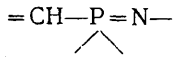
Structure (XCV) with a pentacoordinated phosphorus atom was more stable as the protonated derivative.[167,168]

On the other hand 4,5-benzo-1,3,2-oxazaphospholine (CXXXVIII) was subject in solution to irreversible transition into a form with a lower phosphorus coordination.[68]

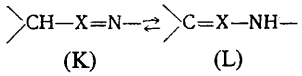


(CXXXVIII) (CXXXIX)

No prototropic conversions have been found in the triad



in the five-membered cyclophosphazene series. 1,2σ^4-Azaphospholines[102–105] and 1,3,4 σ^4-oxazaphospholines[121–128] exist only in the imide form (K). In addition the carbocyclic pyrrole[102] and oxazol-2-one[216] analogues of these compounds have the enamine structure (L).



(K) (L)

4. Complex-forming reactions

The electron-donating character of the phosphazene bond is determined by the extent of hybridisation and other electronic parameters of the orbitals occupied by the unshared electron pair of nitrogen.[137] As has been shown in a series of investigations complex formation of linear phosphazenes with salts of mercury and cadmium,[217] Lewis acids,[218–221] iodine[222] and metal carbonyls[138] leads to coordination at nitrogen.

Complexes of 3,3-diphenyl-1,4,3-oxazaphospholines with stannic chloride of composition 1:1 are known in the cyclophosphazene series with tetracoordinated phosphorus.[128] Complex formation in the ligand is effected at the nitrogen atom according to IR spectral data.

Complex formation of hetero-1,2-azaphospholes with a dicoordinated phosphorus atom has been studied most. Competition of both donor centres is possible in the presence of unshared electron pairs on the phosphorus and nitrogen atoms in the 1,2,3σ^2-azaphosphole molecule. Diaza- and 1,2,4,3σ^2-triazaphospholes gave complexes with metal carbonyls where the dicoordinated phosphorus atom was the donor.[223,224] It has been recorded that 1,2,3σ^2-diazaphospholes display weaker donor properties than triazaphospholes. This is linked with the change in degree of orbital hybridisation of the unshared electron pair at phosphorus which is reflected in the size of the endocyclic angles being reduced on going from a triaza- to a diazaphosphole.

Coordination at phosphorus was observed when forming a complex of 2-methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (α-isomer) with compounds of trivalent gold.[225] However the phosphazene bond does not participate in complexes of the β-isomer and the role of donor is played by the neighbouring nitrogen atom. Seemingly, complex formation of 1,2,4,3σ^2-triazaphosphole with boron trifluoride also occurs without participation of σ^2-phosphorus.[75,77,226,227]

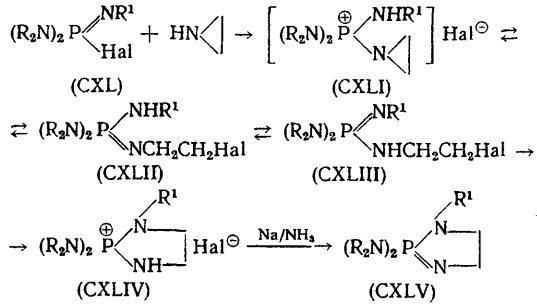
Salts of copper, mercury and cadmium gave solid complexes with 1,2,4,3σ^2-triazaphospholes which have not been studied in detail.[77]

Significant success in developing the chemistry of cyclophosphazenes has been achieved in a comparatively short period. To date the main synthetic routes and chemical transformations of five- and six-membered representatives of these cyclanes have been determined. Rules for the display of their reactivity as a function of structure have been elucidated. There is no doubt that investigations will be extended to larger and smaller rings. There is interest both for the development of theoretical organic chemistry and for purpose-directed hetero-organic synthesis.

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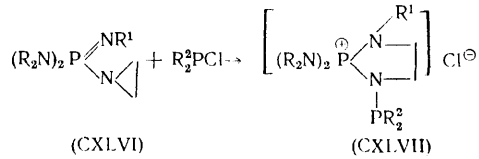
Since preparing the manuscript for printing additional information has appeared on the problem under consideration.

Synthesis of 5-membered cyclophosphazenes. A set of studies has been published recently by Pinchuk, Marchenko and co-workers on the synthesis of 1,3,2-diazaphospholines (CXLV).[228–232] The proposed method is based on the reaction of halodiaminophosphazenes (CXL) with ethylenimine.



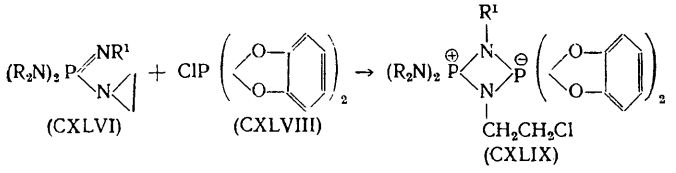
(CXL) (CXLI) (CXLII) (CXLIII) (CXLIV) (CXLV)

Bromodiamidophosphazenes (CXL) are significantly more reactive than the corresponding chloro derivatives. It was shown using the latter that the formation of diazaphospholidinium salts (CXLIV) was a complex process of reversible conversions of the intermediates (CXLI)–(CXLIII).[228] A modification of the indicated reaction was the interaction of aziridinodiaminophosphazene (CXLVI) with a P(III) monoacid chloride.[232]



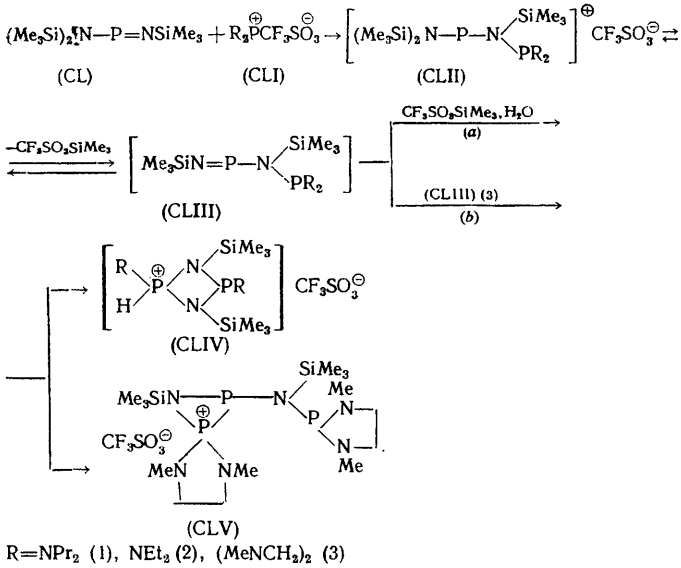
(CXLVI) (CXLVII)

However chlorophosphorane (CXLVIII) unexpectedly adds to phosphazene (CXLVI) with the formation of bonds directly onto the two nitrogen atoms, viz. the imidine and the aziridine.[233]



(CXLVI) (CXLVIII) (CXLIX)

Compounds (CXLIX) represent a new type of diazaphosphetidine containing differently charged tetra- and hexacoordinated phosphorus atoms. The reaction between phosphazenes (CXLVI) and P(III) diacid chlorides proceeds by the same route with the formation of diazaphosphetidines containing tetra- and tricoordinated phosphorus atoms.[234] The reaction of acyclic phosphazene (CL) with phosphenium trifluoromethylsulphonate (CLI) leads to the analogous heterophosphocyclane (CLIV).[235]



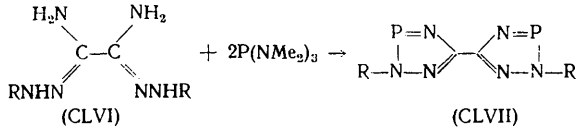
(CL) (CLI) (CLII) (CLIII) (CLIV) (CLV)

R=NPr$_2$ (1), NEt$_2$ (2), (MeNCH$_2$)$_2$ (3)

Compounds (CXLIV), (CXLVII), (CXLIX), (CLIV) and (CLV) are salts of the corresponding five- and four-membered cyclophosphazenes with a significantly polarised P=N bond. The fairly high stability of the indicated salts supports this.

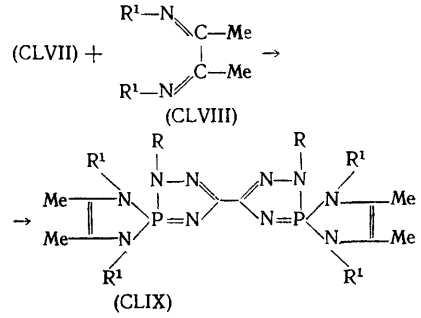
Investigations on the synthesis of hetero-1,2σ^4-azaphospholines by the [3 + 2]-cycloaddition of isocyanates of P(III) acids to dipolarophiles have continued. Examples of the latter which have been studied are chloro-substituted acetaldehydes,[236] hexafluoroacetone, esters of trifluoropyruvic acid,[237] diphenylcarbodiimide[238] and a series of other reactants containing a C=N bond.[239]

New bicyclic 1,2,4,3σ^2-triazaphospholes (CLVII) have been obtained in [4 + 1]-cycloaddition reactions.[240] The skeleton of bicycle (CLVII) is constructed on the basis of the diamidrazone molecule (CLVI), both ends of which are subject to cyclisation under the action of a triaminophosphine.



(CLVI) (CLVII)

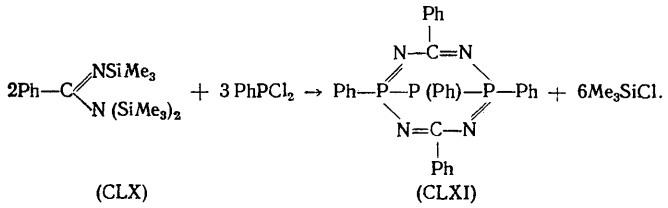
Triazaphospholes (CLVII) react further with di-imines (CLVIII) with retention of the P=N bond and the formation of new bis-spirobicyclophosphazenes (CLIX).



(CLVII) (CLVIII) (CLIX)

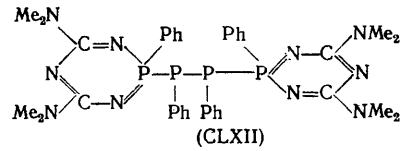
Synthesis of 6-membered cyclophosphazenes. The interaction of *C,N*-diarylnitrilamines with isocyanatophosphites has been studied in continuation of investigations on the [3 + 3]-cyclocondensation reaction.[241,242] New representatives of 1,2,4,5σ^4-triazaphosphorines (LXVII) (Table 4, example 2) have been obtained.

An interesting type of bicyclic diazatriphosphorine (CLXI) is formed by the reaction of phenyldichlorophosphine with silylated amidines (CLX).[243]



(CLX) (CLXI)

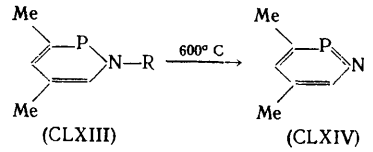
The reaction of phenyldichlorophosphine with dimethylguanidine hydrochloride in the presence of triethylamine leads to an analogous compound.[243] Bicyclic triazaphosphorine (CLXII), in which the rings are separated by a chain of four phosphorus atoms, was described in the same paper.



(CLXII)

The molecular structure of the triazaphosphorine ring in 2,2-bis(aziridinyl)-4,6-bis(trifluoromethyl)-1,3,5,2-triazaphosphorine has been studied.[244]

Synthesis of six-membered cyclophosphazenes (CLXIV) with dicoordinated phosphorus has been effected by vacuum thermolysis of azaphosphorine (CLXIII).[245]



(CLXIII) (CLXIV)

R = t-Bu, t-BuCH$_2$CH$_2$CMe$_2$.

In addition to the synthesis of cyclothiophosphazenes (VI) (Table 1, example 5) new types have been isolated by the reaction of lithium enolates of acetaldehyde with triazathiodiphosphazenes.[246]

Some problems of the chemistry of cyclophosphazenes, viz. isomerisation and tautomerism, have been considered in a review.[247]

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Perfluorinated carbon-chain copolymers with functional groups and cation exchange membranes based on them: synthesis, structure and properties

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ABSTRACT. The review is devoted to perfluorinated polymers with sulphonic and carboxylic acid groups and to cation exchange membranes based on them. The synthesis is described of copolymers of tetrafluoroethylene with perfluorovinyl ethers containing functional groups by radical copolymerisation in an organic medium and in aqueous emulsions. Special features of the copolymerisation and approaches to obtaining copolymers with set characteristics are discussed. Data are presented on the structure and physicochemical properties of the polymeric films. Attempts to form membranes from the polymers obtained, the means of strengthening them and methods for chemical modification are described. Data are correlated on the influence of structure and polymer composition and the nature of the functional groups on the electrochemical characteristics of membranes. Special features of the functioning of perfluorinated membranes in the process for making chlorine and alkali by the electrolysis of sodium chloride solution are considered.

The bibliography has 104 references.

Contents

I. Introduction 560
II. Synthesis and macromolecular characteristics of copolymers with functional groups 560
III. Physicochemical properties of copolymers 564
IV. Membrane formation 568
V. Chemical modification of membranes 568
VI. Electrochemical properties of membranes 570
VII. Conclusion 572

I. Introduction

Perfluorinated carbon-chain polymers occupy an important place in the wide range of carbon chain polymers. The presence of fluorine atoms in the main chain causes unique chemical stability and high thermal sturdiness for materials prepared from these polymers. The combination of such properties has aided wide application of perfluorinated polymers (PFP) [primarily polytetrafluoroethylene and copolymers of tetrafluoroethylene (TFE)] in various areas of science and technology.[1]

The creation of ion exchange materials based on copolymers of TFE with perfluorovinyl ethers (PFVE) containing functional groups has extended the areas of application of PFP still more. With the aid of cation exchange membranes (CEM) prepared from PFP a process has been established for obtaining alkali and chlorine by the electrolysis of concentrated aqueous solutions of sodium or potassium chloride (the so-called "chlorine–alkali" electrolysis) by membrane technology. This process has given the most powerful impulse to the development of cation exchange membranes from PFP, to the technology of preparing them, and also to the investigation of the structure and properties of such materials. The problem posed was therefore that of developing CEM with a high chemical stability and mechanical sturdiness, low electrical resistance and high selectivity.

The results of such developments are reflected in the large number of patents published in the seventies and eighties by several companies from the USA (Dupont) and Japan (Asahi Chemicals, Asahi Glass, etc.). The total energy consumption on obtaining chlorine and alkali in an electrolysis plant using CEM is 25–40% less than in traditional methods of electrolysis with mercury and diaphragms.[2] The replacement of mercury by membranes in plant is exceptionally important from the ecological point of view apart from anything else.

The use of perfluorinated CEM is not restricted solely to the chlorine–alkali electrolysis process. They are used in a whole range of electrochemical processes[3,4] and their sphere of application is widening precipitately.

The correlation of information enabling a linking of the special features of membrane function in various processes with the structure and properties of the polymers from which they were prepared and with the conditions of forming and modifying films of these polymers, will stimulate further development of new polymers and membranes and will enable the limits of their application in practice to be extended.

II. Synthesis and macromolecular characteristics of copolymers with functional groups

The creation of CEM both for chlorine–alkali electrolysis and for other processes is a complex problem. It comprises a series of necessary and inseparably linked steps. The first is the synthesis of suitable perfluorinated monomers with functional groups, the second is the development of conditions for the copolymerisation of TFE with these monomers, the third is the obtaining of membranes from the prepared polymers, including stages of making the films, strengthening them and modifying them chemically.

1. Selection of monomers

The synthesis of monomers for obtaining PFP with ion exchange groups is a vast self-contained area of organofluorine chemistry in which intensive investigations are being conducted continuously. Several tens of monomers have been patented but only a few of them are used in practice.

PFVE of the following general formula are used as monomers with functional groups and are copolymerised with TFE:

$$CF_2=CF-O-(CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O)_m-(CF_2)_n-X \quad \text{(A)}$$

where usually m = 0 to 2, n = 1 to 4, X is SO_2F, SCH_2H_5, $COOCH_3$. The group X then changes to the ionic form SO_3^- or COO^- in the obtained copolymers.

The first PFVE of the indicated type was perfluoro-(4-methyl-3,6-dioxa-7-octene)sulphonyl fluoride (I):

$$CF_2=CF-O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O-CF_2-CF_2-SO_2F \quad \text{(I)}$$

The sulphonic cation exchange membrane 'Nafion' was made based on its copolymers with TFE. Monomers developed later have also acquired great practical importance, e.g. methyl perfluoro-(5-oxa-6-hepten)oate (II),

$$CF_2=CF-O-CF_2-CF_2-CF_2-COOCH_3, \quad \text{(II)}$$

methyl perfluoro-(6-methyl-5,8-dioxa-9-decen)oate (III)

$$CF_2=CF-O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O-CF_2-CF_2-CF_2-COOCH_3 \quad \text{(III)}$$

perfluoro-(4-oxa-5-hexene)sulphonyl fluoride (IV)

$$CF_2=CF-O-CF_2-CF_2-CF_2-SO_2F, \quad \text{(IV)}$$

and perfluoro-(5-methyl-4,7-dioxa-8-nonene)sulphonyl fluoride (V):

$$CF_2=CF-O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O-CF_2-CF_2-CF_2-SO_2F \quad \text{(V)}$$

The routes of synthesis of the main monomers have been published.[5]

In addition to those listed PFVE containing two carboxyl groups,[6] and perfluoroallyl ethers with functional groups[7] have been proposed in the patent literature. Several other monomers described in patents do not introduce any changes in principle into the composition and structure of the ion exchange materials based on them compared with polymers synthesised from compounds (I)–(V) and differ only in method of synthesis. For example it has been proposed to use PFVE for the synthesis of ion exchange materials which have formula (A) where X is a ketone of structure $-C(O)-CF_3$ or $-C(O)-CH_3$ [8] or X is ω-hydroperfluoropropylvinyl ether $CF_2=CF-O-CF_2-CF_2-CF_2H$.[9] The side groups of the units of these monomers were oxidised to carboxyl groups in the copolymers obtained with TFE.

The preparation of PFVE containing ionogenic groups for phosphonic acids has been described.[10] However the complexity of synthesising such monomers precludes discussion of their practical application at present. Finally PFVE have been patented[11] differing in the replacement of the CF_3 group in them by CF_2Cl which affords additional possibilities for modifying the obtained PFP.

As a third comonomer the use of PFVE containing no functional groups, e.g. $CF_2=CF-O-CF_2-CF_2-CF_2-CF_3$, has been recommended in the copolymerisation of functional PFVE with TFE. Their introduction improves the physico-mechanical properties of films.[12–14] The possibility of using ethylene or other olefins as a third comonomer has been mentioned.[15]

The method of strengthening the polymeric material of membranes by cross-linking by introducing perfluorinated compounds with two vinyl groups as comonomer with PFVE at the polymerisation stage has been discussed in many patents.[13,16–18] However this method has not been used in practice probably because of the difficulty of forming films from the cross-linked polymers and also because of the poor availability of monomers of that kind.

2. Special features of the radical copolymerisation of vinyl ethers with tetrafluoroethylene

Copolymers of PFVE and TFE are obtained by radical copolymerisation. Vinyl ethers, particularly when perfluorinated, have an extremely low reactivity on copolymerisation with TFE. The shape of the curve describing the dependence of copolymer composition on the composition of the monomeric mixture (Fig. 1) indicates that on copolymerisation (II) and (III) require to be in considerable excess in relation to TFE in order to obtain polymers with an appreciable content of PFVE units. The curves for the dependence of polymer composition on the composition of the monomer mixture when copolymerising TFE with PFVE (IV) or (V) have a similar shape.[20] The copolymerisation constants calculated by the Fineman–Ross method for ethers (II) and (III) were 0.14 and for TFE 7.0.[19] Close values for the copolymerisation constants were also obtained for sulphonyl fluoride monomer (V) and TFE, 0.08 and 8.0 respectively.[5] Calculation of the parameters of the Alfrey–Price equation gave values of Q (a parameter proportional to the degree of double bond conjugation with substituents) and of e (a parameter reflecting the excess charge of the monomer caused by the polarising influence of the substituents) for carboxyl-containing PFVE equal to 0.0057 and 1.08 while values for Q and e for TFE were 0.089 and 1.22 respectively.[21] Such appreciable differences in the size of parameter Q, i.e. in the activity of TFE and ether,

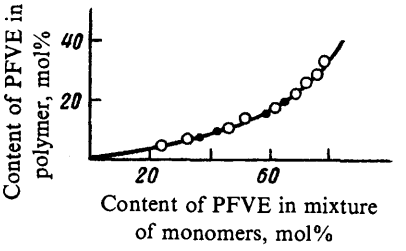


Figure 1. Dependence of copolymer composition on the composition of the mixture of monomers in the copolymerisation of PFVE (II) or (III) with TFE alone at 70 °C.[19]
○ Experimental data for PFVE (II), ● ditto for PFVE (III).

significantly complicate the synthetic process for copolymers of a given composition and demand careful observation of the experimental conditions, particularly the maintenance of a precise concentration ratio between the comonomers during the whole experiment.

Another special feature of the process of copolymerising PFVE with TFE, which is essentially reflected in the molecular weight (MW) and molecular weight distribution (MWD) of the obtained polymers, is linked with a fragmentation reaction of the radical of the terminal unit of a monomer ether:

$$\sim CF_2-\dot{C}F \longrightarrow \sim CF_2-\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}-F + R_f-\dot{C}F_2 .$$
$$\quad\quad\quad

pressure limit indicated in patents is 0.7 MPa but mostly copolymerisation in an emulsion is carried out at a TFE pressure of 1.4–2.0 MPa.[17]

The most important advantage of emulsion copolymerisation over polymerisation in an organic medium is the possibility of conducting the process up to a high conversion of the ether monomer. At conversions above 45% polymerisation at constant TFE pressure does not provide consistency of composition for the obtained polymer. This consistency may be achieved only in a regime of an automatically regulated reduction in TFE pressure according to the reduction in PFVE concentration.[21]

It should be noted that the emulsion polymerisation process makes it possible to obtain copolymers with a higher MW and provides a better reproducibility of results compared with polymerisation in non-aqueous medium. However it presents exceptionally high requirements both in precision of maintaining technological parameters and in the purity of all components.

One of the requirements is the maintenance of the necessary pH value of the aqueous phase since the extent of hydrolysis of the ester groups on the functionalised monomer depends on it (Fig. 2). The appearance of carboxyl groups in the polymer as a result of hydrolysis leads to an abrupt worsening of its reprocessability by reason of an appreciable increase in pour point due to generated hydrogen bonds. Carboxyl groups may also be formed on hydrolysis of the terminal acyl fluoride groups resulting from rearrangement of the ether monomer radical as a result of the fragmentation reaction (1). Consequently, before reprocessing, copolymers obtained by the emulsion method are treated with methanol[28] with the aim of re-esterifying carboxyl groups.

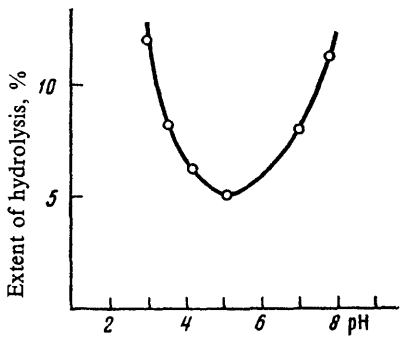


Figure 2. Influence of aqueous phase pH on the extent of hydrolysis of monomer (II) ester groups during emulsion copolymerisation.[21]

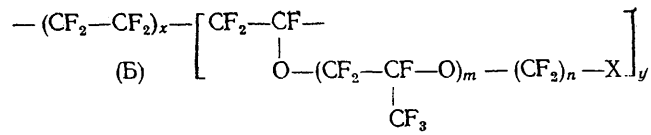
The regulation of copolymer MW is achieved by introducing aliphatic hydrocarbons or alcohols into the medium,[18] i.e. by methods traditional for obtaining fluoropolymers. Agents for chain transmission reduce the contribution of the fragmentation (1) of the growing radical. Stable hydride groups, viz.-CF_2H, are formed in place of terminal acid fluoride groups.[1]

On isolating the polymer obtained by emulsion polymerisation quantitative extraction of unreacted PFVE with freon CF_3CCl_3 from the latex has been proposed[21] followed by purification by distillation with addition of agents preventing thermal polymerisation. Treatment of the latex with freon has a second purpose, viz. removal from the copolymer of its lowest molecular portion.[29]

The emulsion copolymerisation of TFE and sulphonyl fluoride monomers has been patented very recently.[30–33]

5. Copolymer composition

The composition of copolymers used as materials for making perfluorinated CEM is expressed by the following formula:



where x and y are the molar fractions of TFE and PFVE units respectively. Due to the low reactivity of functionalised PFVE, units of it are distributed statistically in the copolymer on polymerisation and do not form blocks.

The ratio of TFE and PFVE units determines the whole complex of physicochemical, mechanical and electrochemical properties of the membranes prepared from the obtained copolymers. The molar proportion of the units of functionalised monomer in the copolymer may be varied over extremely wide limits from 5 to 30 mol.%.[18] The optimum content of PFVE with ionogenic groups in copolymers was from 8 to 15 mol.%. At a lower content membranes have high electrical resistance and low ion exchange capability. The preparation of films of such copolymers is difficult due to the high reprocessing temperature. Films of copolymers with a content of PFVE units bearing ion exchange groups greater than 20% swell excessively in solutions of electrolytes.

The homogeneity of macromolecules of the obtained copolymer is important. The content of ionogenic units in a copolymer must not deviate more than 0.3 mol.% in either direction for reproducibility of the electrochemical characteristics of membranes obtained from various batches of copolymer.[21]

If a non-ionogenic perfluoroalkylvinyl ether is introduced into the copolymer its molar proportion comprises from 2 to 20%.[18] It was shown in the same study that the molar ratio of units of ethylene or other olefin to TFE may be varied from 1:9 to 6:4.[18]

The terms "equivalent weight" (EW) and "exchange capacity" (EC) are used for the characterisation of the composition of copolymers of TFE and PFVE with ion exchange groups. The equivalent weight is the molecular weight of polymer corresponding to one ion exchange group and the exchange capacity is the quantity of milligram-equivalents of ion exchange groups contained in 1 g dry polymer. The exchange capacity of a copolymer is greater the greater the molar portion of monomer with ion exchange groups in it, and at equal molar proportions of such units the EC grows with the reduction in MW of the functionalised monomer. The equivalent weight and exchange capacity are inversely proportional, EC = 100/EW. The values of EW lie as a rule in the range 500–2000 and of EC 0.5–2.0 mg-eq/g.

6. Molecular weight and molecular weight distribution of copolymers

There are practically no data in the literature concerning the macromolecular characteristics of copolymers of the described type which is due, firstly, to the considerable methodological difficulties in determining them and secondly to the fact that not all the scientific results obtained in the industrial laboratories of companies are reflected in publications.[12]

Methodological difficulties are caused by the difficulty of obtaining solutions of copolymers which are suitable for MW determinations. Some results of MW determinations have been reported.[21] According to the report MW values of copolymers of (II) with TFE lie within the limits 10^5-10^6, however these data also were obtained by an indirect route. The copolymer of TFE with (II) is insoluble in accessible solvents but the copolymer of TFE with $CF_2=CF-O-(CF_2)_3-COOC_{10}H_{24}$ is soluble in chlorobenzotrifluoride. The MW of the copolymer containing decyl groups may therefore be measured by osmometry. The values of copolymer MW obtained in this way were extrapolated to the copolymer of (II) with TFE which was synthesised under analogous conditions and used in membrane preparation.

As a result of the difficulty of determining MW directly for copolymers of PFVE with TFE the size of T_Q, linked with the melt viscosity, was introduced for assessing practically the MW of carboxyl-containing copolymers.[16] T_Q is the temperature at which the polymer melt flows at a rate of 100 mm^3/sec through a nozzle of diameter 1 mm and length 2 mm at a pressure of 3.0 MPa. A linear relationship was established between T_Q and log MW of the copolymer determined by the indirect method indicated above (Fig. 3). For polymers used for obtaining cation exchange membranes T_Q lies within the limits 180–300 °C.[17] Polymers with a lower T_Q, i.e. with a lower MW, do not give films with a sufficiently high mechanical strength and polymers with higher T_Q values are difficult to reprocess.

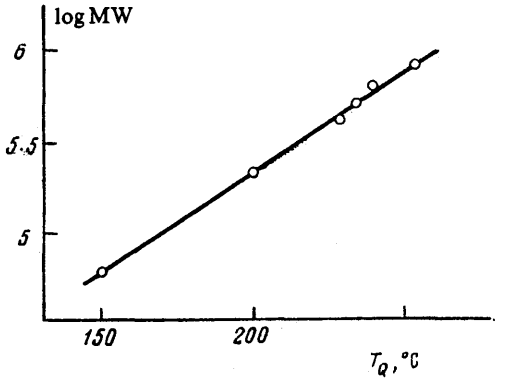


Figure 3. Relationship between T_Q of copolymers of (II) with TFE and their MW.[21]

There are no literature data on the MW of copolymers with sulphonyl fluoride or sulphide groups. It transpired that copolymers used for preparing membranes must possess high MW.[5,12] The required order of MW has been assessed[27] at the same value as in the case of carboxyl-containing polymers, i.e. 10^5-10^6.

There is even less information on the MWD of ion exchange PFP although this parameter may influence in a significant way the physico-mechanical and electrochemical properties of the membranes obtained from them. There are only hints that the synthesised PFP must have a narrow MWD. One of the purposes of MW regulators is to reduce the polydispersity of macromolecules.[18] The extraction of a copolymer with boiling freons under pressure enables removal of low molecular fractions and a narrowing of the MWD of a sample which improves the technological characteristics of the obtained membranes.[29]

III. Physicochemical properties of copolymers

The structure, physicochemical and electrochemical properties of perfluorinated CEM with sulphonyl groups based on copolymers of (I) with TFE (Nafion) have been investigated to a much greater extent than have the properties of other copolymers with carboxyl and sulphonyl groups developed later. The results of investigations of physicochemical properties of copolymers have been correlated.[34] Crystallinity, physico-mechanical properties and hydrophilicity exert an appreciable influence on the operating characteristics of CEM.

1. Crystallinity

The methods of investigating the supramolecular structure of the CEM Nafion (low-angle scattering of X-radiation and neutrons, IR spectroscopy, NMR) and the data obtained have been discussed.[35] A study has been devoted to the application of the X-ray diffraction method to the investigation of the structure of perfluorinated CEM with sulphonyl and carboxyl groups based on copolymers of TFE with (I).[36] Comparison of the results obtained for copolymers as sulphonic acids and for the same polymers in which the terminal $-CF_2SO_3H$ groups have been converted into carboxyl groups (Table 2) show that firstly the copolymers with sulphonyl groups with the same content of functionalised monomer units and identical length of side chain carrying the ion exchange group have a lower crystallinity than carboxyl containing copolymers. This may be linked with the stronger electrostatic repulsion of the sulphonyl groups characterised by a lower pK_a compared to carboxyl groups.[21] Secondly the degree of crystallinity of a copolymer falls with an increase in the content of PFVE units.

Table 2. Extent of crystallinity of copolymers of (I) and TFE as a function of their composition and type of ion exchange group.[36]

Composition		Extent of crystallinity (%) of copolymers with groups	
EW	(I), mol%	$-CF_2SO_3H$	$-COOH$
1100	13.3	12	18
1150	12.5	—	20
1200	11.7	19	23
1400	9.5	20	27
1500	8.7	22	28

Data on large-angle X-ray diffraction for copolymers of (II) with TFE also show a reduction in the degree of crystallinity with an increase in the proportion of ether monomer units.[37] Copolymers containing more than 20 mol.% monomer (II) are almost completely amorphous.

Crystallinity falls on hydrolysis of the nonionic ($-CF_2SO_2F$ or $-COOCH_3$) to the ionic form of the functional groups. The copolymers of (II) or (III) with TFE have a higher crystallinity as methyl esters than as sodium salts (Fig. 4).

Data on large-angle X-ray diffraction permit the conclusion that the crystal lattice of PFP with functional groups is, in essence, a crystal lattice of polytetrafluoroethylene with large disturbances of packing and is built of consecutive TFE units in the chains of the macromolecules.[21,38] This confirms the dependence of the degree of

crystallinity of copolymers on the proportion of TFE units in them recorded above. As analysis showed,[39] the copolymers are characterised at room temperature by larger intermolecular distances in the crystalline phase than polytetrafluoroethylene. It has been established[40] that these distances are reduced on increasing the EW of the copolymer, i.e. on reducing the PFVE portion, to a value close to 0.566 nm which is characteristic of the crystal lattice of polytetrafluoroethylene at room temperature.

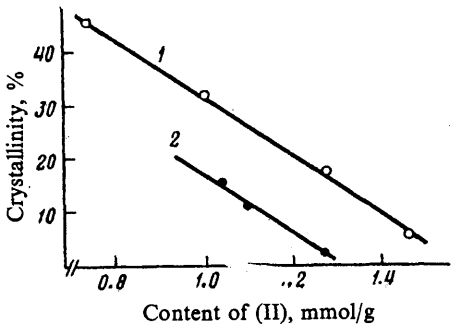


Figure 4. Relationship of crystallinity of copolymers of (II) with TFE on PFVE (II) content.[21]
1, Copolymers with $COOCH_3$ groups; *2*, copolymers with COONa groups.

Attempts to construct a model of the submicro structure of perfluorinated CEM based on the various experimental data, primarily on low-angle X-ray diffraction data, have arisen in the work of Gierke.[41] He has proposed a so-called cluster-channel model according to which hydrated ionogenic groups and counter ions form fairly voluminous (~5 nm in size) associates ("clusters"). Separate hydrated functional groups, forming "ion channels", participate in the transfer of ions and water molecules between such associates. This model has been developed subsequently.[42–44]

An alternative model of the submicro structure of perfluorinated CEM is based on representations of the comb-shaped structure of the copolymers comprising them.[45]

It was shown[46] that the structure of the sulphocation exchange membranes based on copolymers of (I) with TFE does not depend on the presence of low molecular polymer fractions. The latter are concentrated in the amorphous portion of the matrix from where they may be extracted with solvent (freon).

2. Physico-mechanical properties

The physico-mechanical properties of copolymers (viscosity, strength, elasticity) influence in an appreciable way both the processes of forming membranes based on them and on the operating characteristics of membranes.

The dependence of melting point of copolymers of (I) with TFE on content of TFE units proved to be linear (Fig. 5). Extrapolation of the line to 100% TFE content gave a value close to 326 °C, the melting point of polytetrafluoroethylene.

The viscosity of polymers is extremely sensitive to the presence of intermolecular bonds. The appearance in PFP molecules of carboxyl groups able to form hydrogen bonds sharply increases the temperature required for reprocessing and the melting point of such polymers becomes greater than their decomposition points.[21]

Physico-mechanical properties and their link with the supramolecular structure of polymers serving as material for Nafion membranes have been studied in detail.[47] Films of perfluorinated carboxyl-containing copolymers possess several better mechanical properties in comparison with the corresponding copolymers containing sulphonyl groups (Table 3).

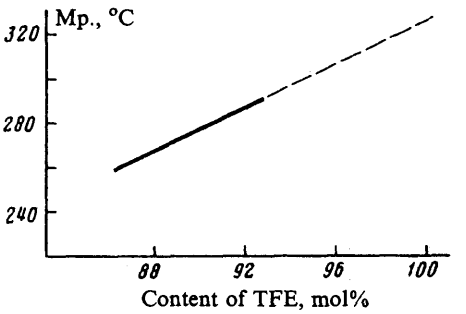


Figure 5. Relationship of melting point (Mp) of copolymers of (I) with TFE to TFE content according to differential scanning calorimetry data.[40]

Table 3. Mechanical properties of films of copolymers of (I) and TFE as a function of the type of ion exchange group.[5]

Property	Ion exchange group	
	$-CF_2SO_3H$	$-COOH$
Tensile strength, kg/cm²	224	236
Specific elongation at break, %	155	253
Modulus of tensile strength, kg/cm²	791	1560

Footnote. Ion exchange capacity of copolymer was 0.03 mg-eq/g, content of monomer (I) units was 0.3 mol.%. Measurements were conducted in aqueous medium at 25 °C.

The high mechanical properties of non-crosslinked perfluorinated copolymers are determined by the crystallites which are formed from sequences of TFE units belonging to different macromolecules. Such crystals with a characteristic spacing ~10 nm provide physical reinforcement to the perfluorinated matrix.[45] In this way the values of the intermolecular distances existing in the crystal at room temperature are achieved in crystals of pure polytetrafluoroethylene at enhanced temperature (200–220 °C).[48] The presence of ionic groups impedes a tighter packing of the indicated fragments in the copolymers. A third monomer, a non-ionogenic perfluoroalkylvinyl ether such as $CF_2 = CFO(CF_2)_3CF_3$, is introduced into the copolymers to reduce the wedging influence on crystals.[49] The relatively long perfluorinated radical in this comonomer causes

buffer zones containing ionogenic groups to form between the crystal and amorphous portions which improves the mechanical properties of membranes.

The form of the functional group proves to have a strong influence on the mechanical properties of functionalised PFP. Thus the strength of carboxyl-containing copolymers as sodium salts is greater than as methyl esters and this difference is increased significantly with an increase in temperature (Table 4). It is seen in Fig. 6, where the specific elongation at fixed tension is shown for these polymers, that at identical load the extension of films of copolymers with terminal $-COOCH_3$ groups is substantially greater than for films of copolymers having $-COONa$ as terminal groups.

Table 4. Tensile strength of films of copolymer of (II) and TFE in relation to temperature and the form of the functional groups.[37]

Temperature, °C	Tensile strength, kg/cm²	
	–COONa	$-COOCH_3$
25	320	250
50	250	40
90	230	7

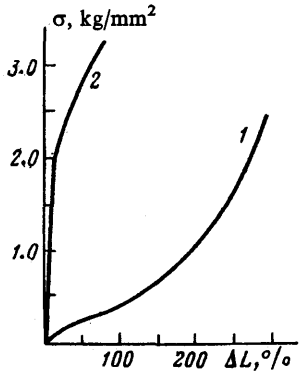


Figure 6. Relationship of stress (σ) and specific elongation (ΔL) for copolymers of TFE with (II) in the form of its *1*, methyl ester and *2*, sodium salt.[37]

Mechanical relaxation spectra permitting determination of phase transition temperatures have been studied for copolymers of (I) with TFE[47] and for copolymers of (II) and (III) with TFE.[50] The glass point of copolymers also depends primarily on the form of the functional group. It is increased substantially on going from copolymers with –COOMe groups to copolymers with –COOH groups and especially with –COONa groups. The glass point falls with increasing content of the number of PFVE units in the copolymer. Thus copolymers of (II) with TFE with –COOMe groups for which EC = 1.25 mg-eq/g has a glass point of 30–35 °C and the same copolymers with EC = 1.80 mg-eq/g only 14–21 °C. These same copolymers with COOH groups have glass points close to 70 °C and its reduction with growth of EC is less significant in this case.

3. Hydration of perfluoropolymers with ion exchange groups

The functional properties of perfluorinated CEM during chlorine–alkali electrolysis are determined to a significant degree by the amount of water absorbed by the membrane since the latter proved to be decisive in the selectivity of the CEM. In the case of a high degree of hydration a reversible migration of hydroxyl ions from the catholyte to the anolyte may occur together with transfer of sodium ions through the hydrated ion channels of the membrane. Water molecules are grouped in the membrane in amorphous regions near ionogenic groups so that the process of water molecule aggregation is determined by the types of ionogenic groups and counter ions (cations) and their interaction (Table 5). In this way the hydrophobic matrix also proves to influence the state of the water molecules in the membrane. IR spectroscopic data make it possible to draw conclusions about the presence of water molecules in perfluorinated CEM which enter hydrate coatings of ions ("bound water") and that found between them ("free water").[38]

The dependence of membrane water content on the type of ionogenic group has paramount importance. Since the electrical polarisability of the COO^- group is greater and of the SO_3^- less than that of a water molecule, COO^- anions (in contrast to SO_3^-) are able to displace water from the hydrated environment of cations.[51] As a result carboxyl containing perfluorinated CEM absorb a substantially lower quantity of water than do sulphonic cation exchange resins (Table 6).

Table 5. Equilibrium water content in copolymers of (I) and TFE with exchange capacity of 1100 for various forms of ion exchange groups.[36]

Ion exchange group	Water content	
	as% polymer dry weight	as number of molecules per ion exchange group
$-CF_2SO_3H$	32	19.6
$-CF_2SO_3Na$	27	16.9
$-CF_2SO_3Cs$	13	8.9
$-CF_2SO_3NHR$	3	2.0
–COOH	6	3.6

Table 6. Equilibrium water content in copolymers of (I) and TFE as a function of their composition and type of ion exchange group.[36]

Composition		Water content			
EW	(I), mol%	% polymer dry weight		number of molecules per ion exchange group	
		$-CF_2SO_3H$	–COOH	$-CF_2SO_3H$	–COOH
1100	13.3	32	6	19.6	3.6
1150	12.5	23	5	14.7	3.1
1200	11.7	20	4	13.3	2.6
1400	9.5	10	3	7.8	2.3
1500	8.7	8	4	6.7	3.0

The reduction in hydrophilicity of copolymers with increase in their EW is linked with the increase in content of hydrophobic TFE units participating in the establishment of the crystal structure.[5,36]

It is seen from Table 5 that sulphonamide groups formed on treating sulphonic cation exchange membranes with amines have a substantially lower degree of hydration (10-fold in comparison with the initial $-CF_2SO_3H$).

A reduction of the length of the side group in PFVE lowers the hydrophilicity of its copolymers with TFE.[52] Therefore copolymers of TFE and $CF_2 = CFOCF_2CF_2SO_2F$ with an EW 800–1300 in the $-CF_2SO_3H$ form contain from 11 to 18 water molecules per ion exchange group in the swollen state which is substantially less than for copolymers of TFE and (I).[53] Such a reduction in hydrophilicity causes a somewhat better selectivity of membranes in the electrolysis process. However copolymers containing $-OCF_2CF_2.SO_3H$ as side group have not been widely adopted due to the complexity of synthesis of the corresponding monomer and due to the occurrence of a cyclisation side reaction in the course of its copolymerisation with TFE.[54]

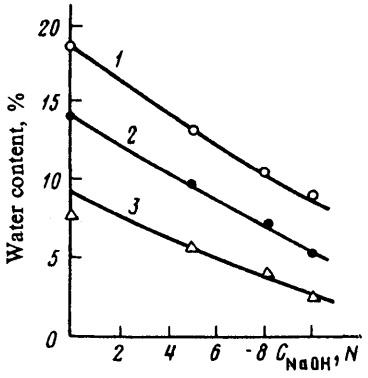


Figure 7. Water content of perfluorinated carboxyl-containing CEM based on modified copolymers of (I) and TFE with EW of: *1*, 1100; *2*, 1200; *3*, 1350 as a function of NaOH concentration.[5]

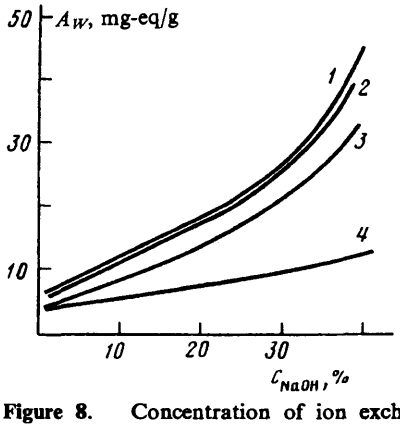


Figure 8. Concentration of ion exchange groups (in mg-eq per gram absorbed membrane water A_W) as a function of alkali concentration for copolymers of (II) and TFE with *1*, EC 1.23 mg-eq/g and *2*, EC 1.44 mg-eq/g, for copolymers of (III) and TFE with *3*, EC 1.21 mg-eq/g and for copolymers of (I) and TFE with *4*, EC 0.82 mg-eq/g.[37]

With an increase in alkali concentration the water content of the swollen polymer is reduced and this effect is strongly expressed for copolymers with a large EC (Fig. 7). Correspondingly with an increase in alkali concentration the effective concentration of ion exchange groups is increased (the mean distance between adjacent ion exchange groups is reduced) due to the reduction in membrane swelling and volume. This effect is displayed more strongly for carboxyl-containing membranes (Fig. 8).

4. Solutions and dispersions of copolymers

The problem of obtaining solutions of perfluorinated copolymers with functional groups is extremely important. Apart from the question of determining copolymer MW and MWD which was referred to above this problem has great value in applications. When solved it would be possible to form membranes by glazing from a solution. In addition the repair of membranes would be substantially simplified. Consequently much attention has been paid to the search for methods of dissolving perfluorinated copolymers. Publications have been devoted to the study of the solubility of copolymers of (I) with TFE and of the swelling of membranes based on these copolymers.[55,56]

Copolymers with CF_2SO_2F and $COOCH_3$ groups pass into solution with great difficulty. They dissolve successfully only in perhalogenated oligomers, perfluorinated kerosenes[57,58] and in perhalogenated compounds with polar groups, such as carboxyl and tertiary amino groups, at high temperatures of 170–220 °C.[58] On cooling these solutions the polymer separated in the form of a solid or gel. At room temperature stable solutions of such copolymers were obtained in saturated perhalogenated ethers simulating the structure of the ether unit of the polymeric chain.[59,60] However similar compounds are expensive and inaccessible.

Conversion of the functional groups ($COOCH_3$ or CH_2SO_2F) into the ionogenic form is alleviated by obtaining solutions of copolymers. Their ability to dissolve increases with an increasing content of ionogenic groups. Thus the hydrolysed copolymer of (I) and TFE containing 16 mol.% monomer (I) units (EW 970) dissolves in ethanol.[61] Copolymers of such type with EW 1100–1200 [11.7–13.3 mol.% of (I)] passed into solution on heating at 250 °C in water–alcohol mixtures under pressure.[61] After cooling to room temperature a 1% solution of copolymer was obtained. It was established that destruction of the polymer did not occur on solution under such forcing conditions. Concentrated (25% or more) solutions of carboxyl-containing copolymers with COOH groups were obtained at room temperature using a mixture of hydrophilic solvents (alcohols, glycols, acetone, methylpyrrolidone, etc.) with a small quantity of water (between 0.05 and 20%).[62] Polymers did not pass into solution in non-aqueous solvents nor on replacing COOH groups by CO_2Me.

Under certain conditions such as when making films, it is possible to use dispersions of polymers in hydrophilic solvents in place of solutions. A method of making such dispersions has been proposed and consists of replacing water in the emulsions obtained after polymerisation by a hydrophilic solvent.[63] Removal of water was effected either by centrifugation before introducing the solvent or after introducing solvent by freezing or by evaporation if the solvent used has a boiling point above that of water. Another method consists of treating the polymer with an aqueous alcoholic mixture at high temperature (180–300 °C) under pressure, the higher the water content in the mixture the higher must be the temperature.[64] The polymer concentration in the dispersion obtained in this way may amount to 2 to 18%.

IV. Membrane formation

The performance of perfluorinated CEM was established at each manufacturing stage including the step of making films from copolymers.

1. Single layer films

The making of films from perfluorinated copolymers is effected before conversion of their functional groups into an ionogenic form since otherwise the temperature required for processing is substantially increased and may reach the decomposition point of the polymer. Preparation of the films is effected by methods traditional for polyfluoroethylene resins. Extrusion at 180–220 °C, i.e. close to T_Q for carboxyl containing polymers, is usually used. Methods of hot pressing or rolling are rarely used.

The thickness of a membrane has almost no influence on its selectivity however to decrease resistance and the resultant energy losses it is desirable to reduce the thickness of a film. Here the mechanical strength proved to be the limiting factor.

The problem of mechanical strength is usually solved by introducing a reinforcing base into a film. Polytetrafluoroethylene fabric is used as such a base for reasons of chemical stability. The film thickness (usually 150–250 μm) must be sufficient such that the reinforcing fabric is encapsulated in the film without disturbing its integrity. The fabric is combined with the film by hot pressing. Such a reinforcement doubles the tensile strength of the membrane with a simultaneous 3- to 4-fold reduction in its ability to stretch (specific elongation at break).[65] Flakes of microporous polytetrafluoroethylene of thickness 13–75 μm and pore size 3–15 μm have been used in place of fabric.[66]

The presence of non-ion exchange strengthening material increases the electrical resistance of the membrane so that one of the problems is to reduce the volume fraction of such material in the membrane. The original method of reinforcing films was suggested in a patent.[67] The copolymer was mixed with a small amount (2–3%) of fibrilar polytetrafluoroethylene, extruded and the obtained film stretched, as a result of which the polytetrafluoroethylene forms an oriented structure confering high stability towards bending and punching to the membrane and the required mechanical strength.

The possibility of using chemical cross-linking for strengthening films has been indicated in several patents, however there are no data on the practical application of this method.

2. Multilayer membranes

The perfluorinated CEM used in the chlorine–alkali electrolysis process consist, as a rule, of two or more layers. There are three main methods of preparing multilayer films.

The first, the chemical modification of the surface layer of one prepared film, will be considered in detail in the next chapter. The second method is the lamination of two or several films. The advantage of the lamination method is that the layers of the ensuing membrane may be prepared separately and independently of one another and each of them may set desired characteristics. This explains the wide application of such a method. The disadvantage of laminated membranes is the risk of their separation during operation. Since one of the layers usually contains a copolymer with carboxyl groups and the other one with sulphonic acid groups, then to reduce the differences (in swelling ability for example) between these layers and to improve adhesion it is possible to introduce between them a layer of a mixture of such copolymers,[68] or to laminate films in one of which the sulphonate groups have been converted into carboxyls.[69] The problem of obtaining multilayer membranes stable towards separation remains, as before, a real one.

The third method of preparing multilayer films, viz. the application onto the surface of an initial film of a glazing from solution, has been used only recently in connection with the successful resolution of the problem of preparing sufficiently concentrated solutions of perfluorinated polymers with ionogenic groups. Thin layers of polymer, not exceeding 15–20 μm as a rule, are usually applied in this way.[68,70,71] Dispersions of polymers may be used in place of solutions, the methods of obtaining them have been discussed above. All three methods enumerated may be applied simultaneously for preparing multilayer membranes.[68]

The reinforcement of twin- or multilayer membranes is usually effected at the lamination stage, by packing the polyfluoroethylene between the two films. In membranes prepared without lamination the reinforcing material is introduced into the thickest layer by hot pressing.

With the aim of reducing the voltage in the electrolytic cell the distance between the electrodes and the membrane is minimised so that electrolysis occurs in the vicinity of the membrane surface. However at a distance of less than 1 mm between membrane and cathode it becomes difficult to remove bubbles of nascent hydrogen which have a tendency to stick to the membrane and lead to an increase in electrolysis voltage.[20] In order to prevent gas bubbles, primarily of hydrogen, sticking to the membrane on its cathode side, membranes for chlorine–alkali electrolysis have recently come to be prepared with rough surfaces. The beneficial effect of a rough membrane surface on the anode side on selectivity, because such a surface aids creation of a thicker diffusion layer, has been described.[72] Many methods of creating a rough surface on perfluorinated CEM have been patented.[15] Best results were given by incorporating fine particles of non-oxide ceramics, usually silicon carbide, into the surface layer on the cathode side and titanium dioxide or zirconium dioxide on the anode side.[68,73,74]

V. Chemical modification of membranes

The functional groups of the PFVE used are in the non-ionogenic form, viz. $-CF_2SO_2F$, $-CF_2SR$ or $-COOR$, at the stages of polymerisation and film formation. Conversion of them into an ionic form is usually brought about after membrane formation by hydrolysis with water or alcoholic alkali. The hydrolysis kinetics of copolymers with sulphonyl fluoride [copolymers of TFE with (I)][75] and with carboxyl groups [copolymers of TFE with $CF_2=CFO(CF_2)_5COOCH_3$][76] have been studied by IR spectroscopy. The energy of activation of the hydrolysis reaction has been determined and is 100 kJ mol^{-1} for copolymers with sulphonyl fluoride groups[75] and 105–140 kJ mol^{-1} for copolymers with carbomethoxy groups depending on the chemical nature of the alkali taken.[76] Moist morpholine was used in place of a solution of alkali for the hydrolysis of the copolymer of TFE with (I).[77] In this case the formation of sulphonamide groups simultaneously with hydrolysis was observed to a small extent.

Chemical modification of polymeric films is also as a rule effected in addition to hydrolysis. The aim of such modification is to enhance the selectivity of membranes by preventing migration of hydrated hydroxyl ions along hydrophilic channels of the membrane from the catholyte to the anolyte. This was sought by creating on the cathode side of the membrane a thin (~2–10 μm) surface barrier layer with a relatively small moisture content.

1. Copolymers with sulphonyl fluoride groups

The first method proposed for modifying membranes of copolymers of TFE with (I) was treatment of their surface (before or after hydrolysis) with ammonia[78] or primary amines.[79] In this the formation of relatively hydrophobic sulphonamide groups (see Table 5) occurs in the surface layer of the film of thickness usually ~10 μm, by the following reaction:

$$R_f—SO_2F + RNH_2 \rightarrow R_f—SO_2—NHR + HF,$$

or, for a polymer previously hydrolysed and converted into the sulphonic acid form,

$$R_f—SO_3H + RNH_2 \rightarrow R_f—SO_2—NHR + H_2O.$$

The use of di- and polyamines permits subsequent cross-linking of the polymer on heating to 100–200 °C by the reactions:

$$R_fSO_2F + NH_2—R—NH_2 \rightarrow R_fSO_2—NH—R—NH_3^+F^-,$$

$$2R_fSO_2NHRNH_3^+F \xrightarrow{\text{heat}} R_fSO_2NHRNHRNHSO_2R_f + HF + NH_4F,$$

$$R_fSO_2NHRNH_3^+F^- + R_fSO_2F \xrightarrow{\text{heat}} R_fSO_2NHRNHSO_2R_f + HF.$$

The formation of a cross-linked structure increases the strength of polymeric films. The course of the indicated reactions has been investigated in detail by IR spectroscopy.[82] The sulphonamide groups resulting from amination have pK_a 8–9 and are completely ionised at pH > 10. In the process of electrolysing a NaCl solution this condition is known to be fulfilled for the aminated layer in the vicinity of the surface facing the cathode. However in electrolysis it is necessary to acidify the anolyte with hydrochloric acid for complete neutralisation of the hydroxyl ions penetrating there. As a result of the proton currents generated in the membrane by this the amino groups in the depth of the aminated layer may appear with a lower effective pH value. The electrical resistance of the membrane then increases sharply. For this reason the use of aminated membranes in chlorine–alkali electrolysis prevents acidification of the anolyte and as a result the chlorine obtained contains no less than 2% oxygen from oxidation of hydroxyl ions at the anode.[5] In addition the sulphonamide groups proved to be insufficiently stable chemically on contact with concentrated alkali.

A method of converting sulphonic acid into carboxyl groups proved to be far more promising from the point of view of improving the electrochemical characteristics of perfluorinated CEM.[5,83] The reaction of sulphonamide groups with anion radicals, for which complexes of sodium with aromatic hydrocarbons such as naphthalene serve as sources, has been proposed for such conversions.[84] Under the action of anion-radicals decomposition of sulphonamide groups occurs with elimination of sulphur dioxide but the generated primary fluorinated amines are unstable and immediately dehydrofluorinate to nitriles which are then subjected to hydrolysis:

$$\sim CF_2SO_2NH_2 \xrightarrow{\text{anion-radicals}} [\sim CF_2NH_2] \rightarrow \sim CF_2N \xrightarrow{\text{hydrolysis}} \sim COOH.$$

This laborious method is however not used in practice.

Many other methods of converting sulphonyl fluoride groups of perfluorinated copolymers into carboxyls have since been patented.[5,83] The most widespread is chemical modification through a sulphinic acid as follows:

$$\sim CF_2SO_2F \underset{(a)}{\rightarrow} \sim CF_2SO_3H \underset{(b)}{\rightarrow} \sim CF_2SO_2Cl \underset{(c)}{\rightarrow} \sim CF_2SO_2H \underset{(d)}{\rightarrow} \sim COOH \qquad (3)$$

The first step [step (*a*)] is usually hydrolysis of the sulphonyl fluoride. Then the $-SO_3H$ group is converted into the relatively more reactive, in comparison with sulphonyl fluoride, sulphonyl chloride by treatment of the polymer with a solution of PCl_5 in $POCl_3$ under fairly forcing conditions (temperature > 110 °C, treatment time > 20 h) [step (*b*)].[85] Step (*c*) proceeds under the action of a reducing agent. Some groups of reducing agents have been proposed, viz. metal hydrides and borohydrides, atomic hydrogen, organometallic compounds, lower valency transition metal salts, etc.[86] The reaction stops at the formation of sulphinic acid when using a weak reducing agent. When using a strong reducing agent and forcing conditions step (*d*), carboxyl group formation, is also effected straight away. We point out that in this case also conversion occurs through the intermediate step of sulphinic acid. A small quantity of sulphinic acid groups is present in the modified polymer and is then oxidised to sulphonate groups with sodium hypochlorite or hydrogen peroxide.[85] The detailed mechanism for step (*d*), the splitting off of two fluorine atoms from the terminal carbon atom under the action of a reducing agent and the formation of a carboxyl group, remains as yet unclear.

A whole series of modifications of the presented scheme exists in which the separate steps may be combined or brought about. Thus the sulphonyl fluoride has been reduced directly to CF_2SO_2H groups with hydrazine, the copolymer with sulphinic acid groups was then subjected to oxidation with molecular oxygen catalysed by variable valency metal ions.

Conversion of sulphonyl chloride to carboxyl groups may be carried out using an oxidising agent and not a reducing agent thus avoiding the sulphinic acid step,[88] for example with molecular oxygen in alcohol medium at high temperature (110–150 °C). Oxidation under forcing conditions, such as with nitrogen oxides or oxygen with UV irradiation at 140–150 °C or a mixture of oxygen and fluorine, permits a one-step process for converting sulphonic acid to carboxyl groups.[88,89]

One further route to obtain carboxyl groups may be represented by the following scheme:[5]

$$\sim CF_2SO_2Cl \xrightarrow[-SO_2]{X_2} \sim CF_2X \xrightarrow{\text{UV + oxidising agent}} \sim COOH, \qquad (4)$$

where X is iodine or bromine. In all cases the mechanism of the final step, in which two fluorine atoms are split off and a carboxyl group is generated, is unclear.

The advantage of the method of modifying functional groups by scheme (3) with reduction of sulphonyl chloride through the step of forming sulphinic acid is its high selectivity.[5] The use of concentrated hydriodic acid in glacial acetic acid as a reducing agent provides a smooth reduction in the proportion of carboxyl groups from 100% to zero in the surface layer of the modified film with a gradient of less than 12% in 1 μm.[85] The gradual change in content across the thickness of the film effectively increases the stability of the membrane towards separation. The kinetics of the chemical modification by the indicated method have been investigated by IR spectroscopy and the energies of activation of the individual steps of the process have been determined.[90]

The chemical modification of copolymers with alkyl sulphide groups (in place of sulphonyl fluoride) is not different in principle. These groups are readily converted by chlorine and oxygen to sulphonyl chloride or may be oxidised directly to sulphinic or sulphonic acid groups.[27]

It should be noted that in the course of converting a sulphonyl fluoride to a carboxyl group a reduction of one occurs in the

sequence of CF_2 units between the ion exchange group and the ether oxygen in the PFVE fragment. Thus from a copolymer of (I) with TFE a polymeric material with $-OCF_2CO_2H$ groups is formed. It has been shown that when only one CF_2 unit is present between the ether oxygen and the carboxyl group stable operation of membranes over an extended period in chlorine–alkali electrolysis is not provided.[5] The reason for this is as yet unclear. It may be connected either with the chemical stability of the terminal groups or with special features of the physical structure of the polymeric material.[5] This has served as a stimulus for the development of new sulphonyl fluoride monomers, including (IV) and (V). After their industrial manufacture was effected, copolymers of (I) with TFE have ceased to be used in practice for obtaining carboxyl-containing ion exchange materials employed in chlorine–alkali electrolysis. At the present time these copolymers are used in chlorine–alkali electrolysis but mainly as sulphonic acids for other purposes.

2. Carboxyl-containing copolymers

Membranes of carboxyl-containing perfluorinated copolymers may be used without any preliminary chemical modification. A procedure for converting carboxyl groups of PFP into sulphonic acid groups has no practical application since the initial monomers with sulphonyl fluoride groups remain more accessible than those containing carboxyl groups.[90]

It is necessary to consider that the pK_a of carboxyl groups of polymeric perfluorocarboxylic acids is 1.9 and membranes of carboxyl-containing PFP may provide cation exchange only at a pH less than 3.[91] Therefore the possibility of adding hydrochloric acid to the anolyte is limited when using cation exchange membranes prepared only from carboxyl-containing polymers in the electrolysis of NaCl solution. Consequently in this case the chlorine obtained contains a certain amount of oxygen as when using membranes with sulphonamide groups. In addition chlorate ion accumulates in the anolyte and is extremely difficult to remove from the brine. Finally the evolution of oxygen at the anode reduces the life time of the latter. On the strength of the above mentioned factors monolayer membranes of carboxyl-containing copolymers are being superseded at the present time by multilayer membranes in which a layer of copolymer with sulphonyl groups possessing high acidity is facing towards the anode.

Polymeric perfluorocarboxylic acids are unstable towards the action of alkali of concentration above 40%.[16] The chemical mechanism of their decomposition under the action of alkali has not been described but it has been reported that sodium carbonate has been detected in the products of decomposition by concentrated sodium hydroxide and $-CF_2H$ groups are found in the polymer.[92] It has also been recorded that with a rise in temperature the alkali concentration sufficient for decomposition is reduced. This effect has been used for generating a surface layer, by short term treatment with concentrated NaOH solution, with a reduced concentration of carboxyl groups facing towards the cathode and consequently with a reduced moisture content. This may be carried out directly in the electrolyser.

3. Other procedures for chemical modification

A whole series of procedures for the chemical modification of perfluorinated CEM has been proposed in the patent literature. In some patents[13,93,94] it is recommended to impregnate membranes carrying sulphonyl groups on one side with carboxyl-containing monomers of various nature (carboxyl-containing dienes[93] or perfluoroacrylic acid[94]) in order to increase their selectivity. Polymerisation is then carried out afterwards. The proposed method[13] of copolymerising TFE simultaneously with other monomers carrying functional groups of a similar nature was ineffective since in this case a uniform material was obtained instead of a twin-layer membrane with a barrier layer.

Many attempts have been undertaken to use graft copolymerisation when obtaining and modifying perfluorinated CEM. The preparation of material for membranes by grafting monomers with ionogenic groups onto PFP, particularly polytetrafluoroethylene primarily by radiation grafting, is tempting in its simplicity. The grafting procedure has been patented.[95] However the most important disadvantage of this method is its non-selectivity. It was recorded[16] that copolymers prepared in this way did not possess the supramolecular structure which makes their use in membranes possible. Radiation grafting has been suggested for use only for modifying fabricated membranes. Thus the selectivity of perfluorinated sulphonic acid membranes is increased by grafting perfluorobutenoic acid on one side of their surface.

The introduction of the other halogens, chlorine, bromine and iodine into polymers as reactive groups in place of fluorine opens further possibilities for the chemical modification of membrane materials. They may be introduced, as indicated in Chapter II, at the monomer synthesis stage. However such a route is extremely laborious and furthermore the reactive groups may prove to have a negative influence on the polymerisation process, by playing a chain transfer role. Consequently it is expedient to carry out such chemical modifications on an already prepared polymer.

Thus a portion of the $-CF_2SO_2F$ groups in the copolymer (up to the stage of forming CH_2SO_2Cl groups) are replaced by $-CF_2I$ or $-CF_2Br$ and then initiation is carried out with peroxides grafting on carboxyl-containing monomers.[97] A similar result was desired when using the reaction of labile halogen atoms with radical initiators containing terminal carboxyl groups.[98] As a result the carboxyl-containing fragments of the initiator are linked with the polymer. Cross-linking of the polymer by the action of peroxide radical initiators at $-CF_2I$ and $-CF_2Br$ groups in place of grafting has been sought.[99] The preparation of a cross-linked structure in copolymers of (I) with TFE using di- and polyamines has been mentioned above.

All the methods enumerated in this section have not as yet been applied in practice to any extent.

VI. Electrochemical properties of membranes

The electrical resistance of membranes used in electrolysis processes must be as low as possible. The electrical conductivity of films and the quantity of water absorbed by them increase simultaneously with increasing content of ion exchange groups in the polymer but with growth in water content the selectivity of the membrane is reduced. The electrical conductivity and selectivity are in inverse relationship. Optimisation of these two parameters is the most important problem in the development of ion exchange membranes.

1. Film conductivity and composition

The dependence of the electrical conductivity of perfluorinated polymeric films on their composition is represented in Fig. 9. Films from carboxyl-containing copolymers have a lower electrical conductivity in comparison with films from copolymers with sulphonic acid groups at a given content of ion exchange groups in

the polymer. It is also evident that at constant EC some increase is observed in specific conductivity with increased comonomer molecular weight. This may be partially linked with the fall in copolymer crystallinity which shows up not only in the mechanical but also in the electrochemical properties of films.[12]

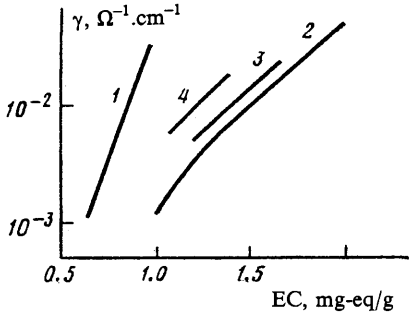


Figure 9. Dependence of electrical conductivity γ of polymeric films on their composition for copolymers of TFE *1*, with (I) in SO_3H form, *2*, with (II), *3*, with $CF_2 = CFO(CF_2)_4COOCH_3$ and *4*, with (III). Curves *2*–*4* in –COOH form.[37]

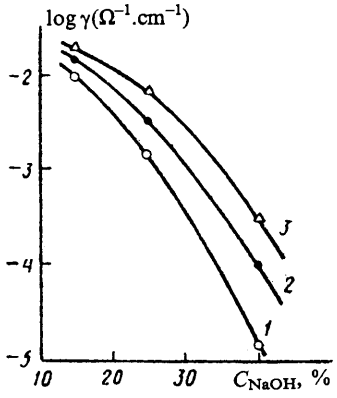


Figure 10. Dependence of electrical conductivity (γ) of carboxyl-containing membranes on NaOH concentration at temperatures of: *1*, 52; *2*, 72; *3*, 90 °C.[37]

The electrical conductivity of perfluorinated CEM depends markedly on the external conditions, viz. alkali concentration and temperature (Fig. 10). The activation energy for the transfer of Na^+ through a membrane of carboxyl-containing polymers at NaOH concentrations of 14, 25 and 40% were 16.4, 38.2 and 71.5 kJ/mol respectively.[37] Such an increase in activation energy with growth in alkali concentration is linked primarily with the reduction in membrane water content, mentioned in Chapter III, depending on the alkalinity of the medium as a result of which the diffusion coefficient of ions is sharply reduced.[38] The indicated effect supersedes the increase in electrical conductivity caused by the increase in mobile ions in the polymer as a result of the non-exchange absorption of electrolyte.

2. Membrane selectivity

The selectivity of perfluorinated CEM has a key significance in their use. The efficiency of using electrical energy, i.e. the proportion of electric current consumed in obtaining the desired products (the so-called yield on current) and also their purity, depends primarily on membrane selectivity in the process of chlorine–alkali electrolysis.

The selectivity of perfluorinated CEM is determined by the degree of "reversible" migration of hydroxyl ions through the membrane from the catholyte into the anolyte which itself depends primarily on the concentration of non-exchange absorbed electrolyte in the membrane. This concentration is significantly lower in the less hydrophilic carboxyl-containing polymers than in copolymers with sulphonic groups particularly at high alkali concentrations (Fig. 11). Since the equilibrium Donnan concentration of hydroxyl ions in the membrane grows with increasing NaOH concentration, cation exchange membranes intended for obtaining electrolytically more concentrated alkali must have a higher density of fixed ionogenic groups. This dependence has been confirmed experimentally. Maximum yield on current is achieved for membranes of higher EC in the case of a higher concentration of alkali in the catholyte.[5,19,83] It has been recorded[16] that membranes of carboxyl-containing copolymers operate with the highest efficiency (yield on current 96–97%) when the concentration of carboxyl groups in the surface layer of the swollen membrane facing the cathode in relation to the water absorbed by it is equal to the alkali concentration in the catholyte. This may be explained by the fact that under such conditions the transfer of Na^+ ions from membrane to catholyte is not accompanied by a change in its degree of hydration. On the basis of this relationship membranes have been developed with various EC of the surface layer for obtaining alkali of various concentration.[93]

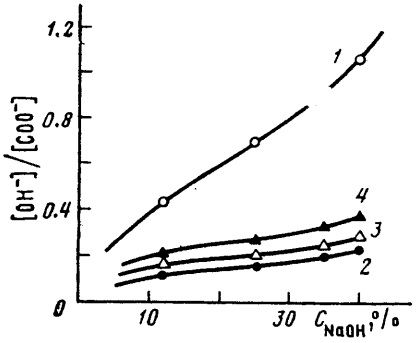


Figure 11. Dependence of hydroxyl ion concentration on alkali concentration at Donnan equilibrium in cation exchange membranes prepared from copolymers of: *1*, TFE and (I) with EC 0.82 mg-eq/g; *2*, TFE and (II) with EC 1.23 mg-eq/g; *3*, TFE and (II) with EC 1.44 mg-eq/g; *4*, copolymers of TFE and (III) with EC 1.21 mg-eq/g.[37]

It is evident from Fig. 11 that films of PFP with sulphonic groups may not possess high selectivity, particularly at high alkali concentrations, and require chemical modification to increase their selectivity or must be used in multilayer membranes having a barrier

layer of polymer with lower water content. The first attempt to prepare such membranes by laminating two layers of copolymers of (I) with TFE having different EC, such as with EM 1100 and 1500,[101] where the second of these layers fulfills a barrier role, was unsuccessful. The selectivity of such membranes was inadequate for their use in industry.[12] Later the analogous method of combining two films of different EC was used to increase the selectivity of membranes prepared from copolymers with carboxyl groups.[102] However as a rule polymer layers bear ionogenic groups of different types in multilayer membranes prepared both by chemical modification and by the lamination method.

Methods of chemical modification of films of ion exchange PFP have been considered in Chapter V. As already mentioned the route to increasing the selectivity of sulphonic cation exchange membranes, by carboxylation of a thin surface layer facing the cathode when fixed in an electrolytic cell, has displaced the method of aminating the surface of these membranes because of the inadequate chemical stability of sulphonamide groups, the increased electrical resistance of the aminated membranes and the difficulties of using them which are linked with the high pK_a of sulphonamide groups. The placing of a barrier layer of carboxyl groups on the surface of the sulphonic cation exchange membrane sharply increases its selectivity without an appreciable increase in electrical resistance. It is shown in Fig. 12 that a barrier layer of thickness 6–8 μm provides optimum selectivity and a further increase in the thickness of this layer did not increase further the yield on current. However the term "thickness of carboxylated layer" remains incompletely defined.[5,83] It is unclear what extent of conversion of sulphonic acid into carboxyl groups is applied as the border of this layer.

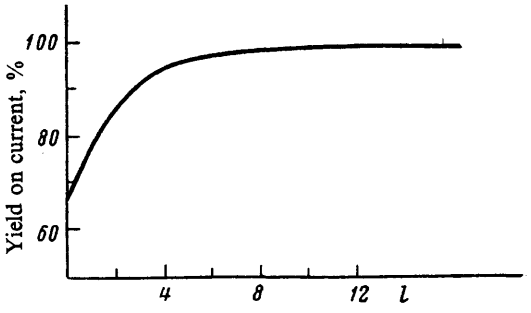


Figure 12. Influence of thickness (l) of carboxylated layer of sulphonic cation exchange membranes on yield on current when using them in the electrolysis of NaCl.[5]

All the highly selective perfluorinated CEM developed recently have a multilayer structure.[68,70,71] Their basic layer, having high EC and consequently low resistance, may be prepared from copolymers both with sulphonic acid[70] and with carboxyl groups.[68,71] In the latter case an additional layer of polymer with sulphonic groups possessing high acidity is placed on the side facing the anode. A relatively thin (10–40 μm) barrier layer of carboxyl-containing copolymer with reduced EC is placed close to the cathode. In membranes intended for preparing alkali of concentrations greater than 40% a further thin layer (~6–20 μm) of polymer with sulphonic groups was created on the side facing towards the cathode in order to protect the carboxyl-containing polymer of the barrier layer from decomposition by the concentrated alkali. It has been applied from a solution but chemical modification procedures may also be used for this purpose.[71] Across such a surface layer a fall of hydroxyl ion concentration occurs to values safe for the carboxyl-containing polymer. It is possible to introduce one more layer to improve the adhesion between layers of polymers of different chemical nature on lamination.[68] The membranes obtained in this way combined high selectivity, low electrical resistance, chemical strength and stability towards film separation.

VII. Conclusion

Great success has been achieved in the last fifteen years in the area of developing perfluorinated CEM as a result of which the industrial process for obtaining alkali and chlorine by membrane technology has been successfully put into practice. At the present time the efforts of many investigators have as usual been concentrated on improving the individual steps of this technology, on simplifying and making more economical the methods of synthesis of monomers used in the manufacture of membrane materials, on the development of methods of obtaining polymers with the desired characteristics by copolymerisation and polymer-like conversion reactions and also on the further development of procedures for fabricating membranes capable of working for an extended time with high efficiency under drastic conditions, on giving them a surface structure providing minimum energy losses during electrolysis, and optimising the parameters of membrane–electrode assemblies, etc. The synthesis of new functionalised perfluorinated monomers remains an urgent problem.

Expansion of the manufacture of perfluorinated cation exchange polymeric materials permits substantially the extension of investigations of their structure and physicochemical properties and, based on this, finding new areas for applying them.

Membranes of PFP with sulphonic groups having strongly acidic properties and providing a high proton mobility were already applied long before chlorine–alkali electrolysis as solid electrolytes in hydrogen–oxygen and hydrogen–halogen fuel cells. With the growth of hydrogen power the use of perfluorinated membranes in the electrolysis of water, where they are able to provide high current density and process efficiency, is extremely promising.[3] One more region for the application of perfluorinated sulphonic cation exchange membranes is that of ion selective electrodes.[4] A review[35] has been devoted to the use of perfluorinated sulphonic cation exchange polymers and 'Nafion' membranes based on them as catalysts. Possessing high acidity they may successfully replace traditional acid catalysts in such processes as hydration, esterification and the alkylation of benzene and its homologues. The use of catalysts based on ion exchange PFP containing metal ions has been considered in a review.[103] There have been communications on the use of perfluorinated CEM for drying gases[4] and for gas distribution.[104]

The uniqueness of the properties of cation exchange PFP and the intensity with which they are being investigated makes it possible to predict with confidence further extension of their spheres of application and an increase in their role in chemical technology.

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αββ-Trifluorostyrene and polymers based on it

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ABSTRACT. The literature data on the synthesis, properties, and applications of αββ-trifluorostyrene and the polymers based on it are surveyed. The characteristic features of the polymerisation and copolymerisation of αββ-trifluorostyrene, the methods of preparation of ion-exchange materials based on polytrifluorostyrene, and their characteristics and applications are examined.

Certain aspects of the effect of fluorine atoms in the vinyl group of αββ-trifluorostyrene on its reactivity and physicochemical properties are discussed. The applications of polytrifluorostyrene-based materials and their advantages are indicated.

The bibliography includes 136 references.

Contents

I. Introduction 575
II. Synthesis and properties of αββ-trifluorostyrene 575
III. Polytrifluorostyrene and αββ-trifluorostyrene copolymers 579
IV. Ion-exchange materials based on polytrifluorostyrene. Their synthesis and properties 582
V. Other aspects of the applications of polytrifluorostyrene 587

I. Introduction

Among the large series of fluorine-containing compounds capable of polymerising, αββ-trifluorostyrene (TFS) occupies a special position by virtue of the combination in its molecule of the perfluorinated vinyl group and the aromatic ring. As a result of this, TFS can be regarded both as a phenyl derivative of tetrafluoroethylene and as a styrene with a perfluorinated vinyl group. Such combination of properties is responsible for a number of characteristic features and for the differences between this monomer and its two analogues both in polymerisation and when they are involved in different chemical reactions.

The polymer obtained on polymerisation of TFS, namely polytrifluorostyrene (PTFS), belongs to the class of thermally and chemically stable materials: it contains a perfluorinated main chain, which is resistant to thermal oxidation, and phenyl substituents. In contrast to polytetrafluoroethylene and the majority of its derivatives, which do not dissolve in any solvent, PTFS is readily soluble in many organic compounds, which permits its processing in different solutions. The presence of the benzene ring in the PTFS molecule ensures the possibility of introducing into it various functional groups and the preparation on its basis of modified materials. This renders PTFS particularly promising for the development of various ion-exchange and other materials with enhanced thermal and chemical stability.

The combination in the TFS molecule of the electronegative fluorine atoms, the vinyl group, and the benzene ring makes it an extremely interesting object for the theoretical study of the effect of electronic structural factors on the reactivity of the unsaturated and aromatic components of this compound and on its physicochemical properties and also on the properties of the monomers based on it.

II. Synthesis and properties of αββ-trifluorostyrene

1. Methods of synthesis of αββ-trifluorostyrene

The first mentions of the synthesis of αββ-trifluorostyrene, a new fluorine-containing monomer, dates back to the end of the 1940s and the beginning of the 1950s when the study by Cohen, devoted to a multistage method of synthesis of this compound, was published.[1,2] The starting materials in this synthesis were the salts or the chlorides or chlorofluoro- or trifluoro-acetic acids:

$$CF_3COCl \xrightarrow[AlCl_3,CS_2]{C_6H_6} C_6H_5COCF_3 \xrightarrow{PCl_5} C_6H_5CCl_2CF_3 \xrightarrow{SbF_3} \rightarrow C_6H_5CFClCF_3 \xrightarrow[\text{abs. ethanol}]{Zn} C_6H_5CF{=}CF_2 .$$

The synthesis is based on the Friedal–Crafts reaction, which results in the formation of the corresponding trifluoroacetophenone or chlorodifluoroacetophenone. The overall yield of TFS does not exceed 30% and the main difficulty is the reaction involving the abstraction of ClF in the last stage of the process.

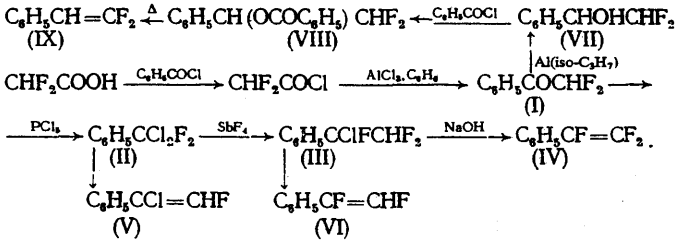
$$C_6H_5COCF_2Cl \rightarrow C_6H_5CCl_2CF_2Cl \rightarrow C_6H_5CFClCF_2Cl \rightarrow C_6H_5CF{=}CF_2 .$$

Table 1. Polymerisation of αββ-trifluorostyrene and its derivatives.[3]

Monomer	Initiator	c_{in}^{*}, %	Polymer, %	T_{soft}^{**}, °C
$C_6H_5CF{=}CF_2$	BP***	9.7	2.9	185–190
(TFS)	BF_3	1.2	0	—
$C_6H_5CH{=}CF_2$	BP	0.4	3.5	176–180
(ββ-DFS)	BF_3	0.4	2.4	127–130
$C_6H_5CF{=}CHF$	BP	0.7	2.7	—
	BF_3	30.0	2.8	225–230
$C_6H_5CCl{=}CHF$	BP	2.7	0	—
	BF_3	3.2	0	—

*c_{in} = initiator concentration.
**T_{soft} = softening temperature of the polymer.
***BP = benzoyl peroxide.

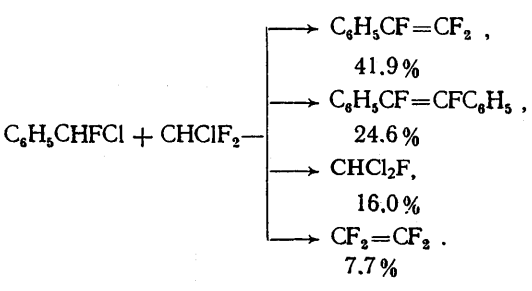
The synthesis of TFS in Prober's study,[3] also dating back to the 1950s, is a development and modification of the method described above. Together with TFS, its derivatives with chlorine and hydrogen atoms instead of fluorine in the vinyl group are obtained by this procedure. These processes can be represented schematically as follows:



All the monomers obtained, with the exception of the chlorine-containing compound (V), are capable of polymerising with formation of polymeric compounds. Table 1 presents data on the polymerisation of these monomers and on the softening temperatures of the polymers based on them.

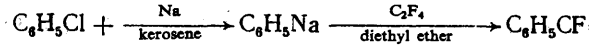
Prober also developed a direct method of synthesis of TFS from chlorotrifluoroethylene and benzene when they are jointly pyrolysed[4,5] in the temperature range 550–600 °C. There is an indication that this reaction can be accelerated by various acid compounds (for example BF_3) and substances with a high specific surface (activated charcoal, $PbMe_4$, etc.).[4] In this method, the reaction mixture is repeatedly circulated through a hot zone with successive enrichment of the mixture in TFS; the mixture is then distilled through a fractionating column with a large number of theoretical plates. A low yield of the final product (not exceeding 30%) and the large amount of side products, which are difficult to remove from TFS because of their ability to form azeotropic mixtures with the latter, must be included among the disadvantages of this procedure (as in the previous methods of synthesis).

Yet another method of the pyrolytic synthesis of TFS consists in the copyrolysis of C_6H_5CHFCl and $CHClF_2$ at 600–800 °C in a stream.[6] The gaseous products obtained are absorbed in scrubbers using water and are fractionated. For the initial proportions of 68.5 mol% of C_6H_5CHFCl and 31.5 mol% $CHClF_2$, the following mixture of products is obtained:

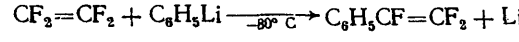


A change in the initial reactant ratio affords other proportions of the final products.

A procedure is also known for synthesising TFS by the reaction of solid PhNa with C_2F_4 in a heterogeneous liquid–solid system containing a solvent for C_2F_4.[7] The reaction is carried out in the presence of an excess of C_2F_4 (whose amount is 50–500%) at a pressure of $(0.7-14)\times10^5$ Pa and in the temperature range from −30 to −100 °C:



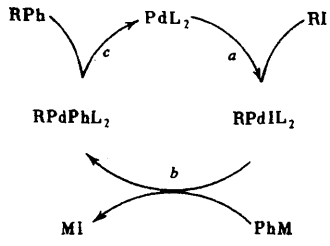
One of the most widely known methods of synthesis of TFS and its derivatives is Dixon's method in which it is obtained via organolithium compounds.[8,9–13]



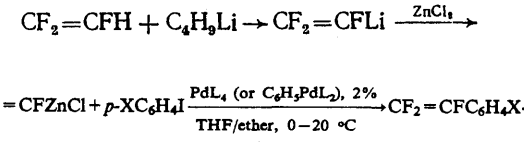
In this procedure, 1 mol of the organolithium compound under an inert atmosphere and in dry diethyl ether at −80 °C is added slowly to 1.2 mol of the fluoroalkene. The yield of TFS by this method also does not exceed 20–30%, since the main product is 1,2-difluorostilbene,[11–14] but the TFS obtained is much purer and its isolation is much simpler.

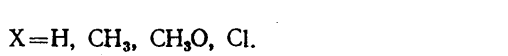
In order to obtain TFS derivatives with substituents in the benzene ring, substituted benzene derivatives were used as the initial organolithium compounds. The corresponding phenyl-lithium derivatives were obtained from them.[13]

Finally a method of synthesis of TFS and its derivatives in a high yield (≥87%) from trifluorovinyl derivatives of lead and zinc and iodobenzene derivatives in the presence of palladium complexes was described recently.[15,16] The method is based on cross-coupling reactions which are known to involve several stages: oxidative-reductive addition (a), transmetallation (b), and reductive elimination (c):[17]



When applied to the synthesis of TFS and its derivatives, this process can be expressed by the general scheme

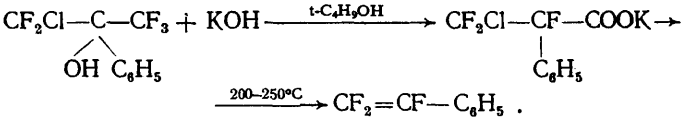




$$X = H,\ CH_3,\ CH_3O,\ Cl.$$

The catalytic reaction involving the coupling of CF_2 = CFZnCl to ArI can be represented as the successive interaction of $ArPdI(PPh_3)_2$ with CF_2 = CFZnCl (exchange reaction) leading to the formation of the complex $ArPd(CF=CF_2):(PPh_3)_2$, which is converted as a result of reductive elimination into the zerovalent palladium complex $Pd(PPh_3)_2$ and CF_2 = CFAr. After the oxidative addition of ArI, the initial complex $ArPdI(PPh_3)_2$ is regenerated.[16] These processes take place in solution in different solvents, the yield of the products increasing as a function of their nature in the following sequence: HMPA ≃ DMF > DMSO > THF > C_6H_6 > $C_2H_4Cl_2$.[15]

In addition, a procedure is known for the synthesis of highly pure TFS using chlorinated 2-phenylperfluoro-2-propanol, from which $CF_2ClCF(C_6H_5)COOK$ is obtained. The latter compound is decomposed at 200–250 °C and 20 mmHg. For example, the synthesis of 1-chloro-2-phenylperfluoro-2-propanol proceeds as follows:



When this method is used, TFS without any impurities is obtained.[18,19]

2. Physicochemical properties of αββ-trifluorostyrene

TFS is a colourless liquid with a specific smell. When stored in air, it gradually decomposes to benzoic acid with liberation of HF.[20] A cyclic dimer is formed readily. This will be described in detail below.

In order to characterise the monomer with the aid of spectroscopic data, one usually employs the UV absorption maximum at 240 nm,[27] the IR absorption band at 1752 cm^{-1} due to the C=C (vinyl) group,[9,27,28] the 1650 and 2000 cm^{-1} bands due to the ring-monosubstituted derivatives, the 690 and 755 cm^{-1} deformation vibration bands,[24] and the 1075 and 1175 cm^{-1} bands due to the CF and CF_2 groups.[24] Table 2 presents certain characteristics of TFS taken from different sources.

Table 2. Physicochemical characteristics of TFS and PTFS.

TFS			PTFS		
property	parameter	refs.	property	parameter	refs.
T_b	133–136 °C (at 760 mmHg)	[4]	T_{soft}	185–190 °C	[3, 21]*
T_b	68–70 °C (at 75 mmHg)	[2, 8]	$T_{g,exp}$	202 °C	[22, 23]**
T_m	−23–−22 °C	[2]	$T_{g,calc}$	204 °C	
Dielectric constant ε	2.56±0.05 in the range 10^2–10^{11} Hz	[24]	Tangent of electrical losses angle tan δ	0.0033–0.0043 at 10^2–10^8 Hz	[24]
Dipole moment μ	1.98 D	[21, 26]			

*Barb[21] used the method of the LSP-limit of the softening point.
**Brown[23] determined the glass point T_g using a scanning calorimeter.

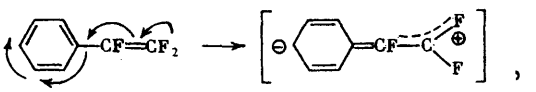
It is known that all non-aromatic fluoroethylene derivatives are coplanar, i.e. all the fluorine atoms lie in the same plane as the double bond.[25,26] On the other hand, the TFS molecule has a non-planar, non-coplanar structure. The *cis*-β-fluorine atom and the *ortho*-hydrogen atom of the benzene ring do not lie in the same plane because the distance between the centres of the hydrogen and fluorine atoms (1.6 Å) is smaller than the sum of their van der Waals radii.[25,26,29]

The results of geometrical calculations are confirmed satisfactorily by the dipole moment of TFS (1.98 D), which indicates the rotation of the trifluoroethylene group relative to the benzene ring and the absence of π-electron interaction between them, as a consequence of which the dipole moment of TFS is identical with those of other fluorinated alkenes, for example, 1,1,2-trifluorooct-1-ene (1.97 D).[25,26] Calculation of the dependence of the dipole moment on the angle between the planes of the benzene and perfluorinated groups showed that the angle in TFS is close to a right angle.[30,31]

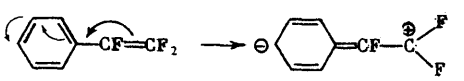
The breakdown of coplanarity in the TFS molecule is also indicated by UV absorption spectroscopic data for this compound. The study of the UV absorption spectra of mono-, di-, tri-, and tetra-substituted derivatives of TFS also lead to the conclusion that the conjugation between the perfluorinated vinyl group and the benzene ring breaks down, which indicates the non-coplanarity of these molecules.[30,31]

One can postulate on the basis of the foregoing that the nature of the effect of fluorine on the electronic structure of the C=C bond in fluorinated ethylenes and fluorinated styrenes is the same. However, analysis of different data permits the conclusion that the fluorine atoms are involved in the π-conjugation of the perfluorovinyl group with the benzene ring. This is demonstrated by the difference in the character of the sulphonation reactions of TFS and PTFS. Whereas the former compound is sulphonated directly with extreme difficulty and the process requires very severe conditions, PTFS can be sulphonated under relatively mild conditions (for example, with chlorosulphonic acid or SO_3 in dry hydrocarbon solvents at temperatures in the range 20–50 °C) (see Section IV).

The presence of conjugation leading to an increased reactivity of the C=C bond, which can be represented schematically by the formula

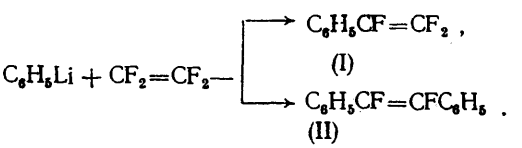


[Presumably intended scheme is:

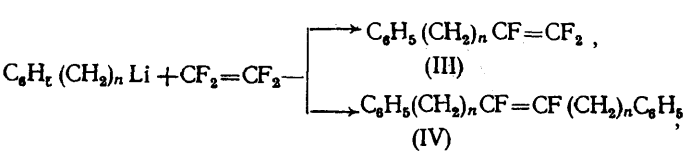


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is believed to be one of the causes of the low yield of TFS (I) in its synthesis via phenyllithium as a consequence of side reactions which result in the formation of a stilbene (II):[11–13]



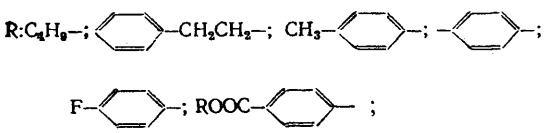
For example, this has been established when one or two methylene groups were introduced into $Ar(CH_2)_nLi$ or when polymethyl derivatives of phenyllithium $(CH_3)_nC_6H_5Li$, where $n > 1$ and CH_3 in in one or two *o*-positions, are used. Judging from the ratio of the products (III) and (IV) obtained by the reaction



when conjugation breaks down, the reactivity of the C=C bond in compound (III) falls, so that the compounds resemble the alkylfluoroethylenes AlkCF = CF_2.[14]

Data concerning the presence of conjugation between the perfluorinated vinyl group and the benzene ring in TFS have also been obtained by spectroscopic methods and have been interpreted on the basis of the available data for the effect of substituents on the electronic spectra and π-donor properties of benzene derivatives.[32]

Interesting data, associated with the presence of conjugation between different groups, have been obtained in the study of the structures, steric effects, the parameters δ and *j*, and other characteristics of TFS by the ^{19}F NMR method.[33–37] Analysis of the NMR spectra of a series of RCF = CF_2 derivatives showed that the change in the δ_{F_1} and δ_{F_2} (β-fluorine atoms) signals is associated with the inductive-resonance effect of the substituents. Thus the shifts of δ_{F_2} diminish in the following sequence:



δ_{F_2}: −7.0 −7.5 −16.3 −17.4 −17.7 −20.8.

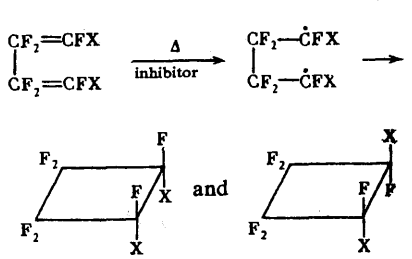
Comparison of the shifts δ_{F_2} for the compounds RCF = CF_2, where R = C_4H_9 or $C_6H_5CH_2CH_2$, with the remaining compounds shows that the greatest changes occur for the β-fluorine atoms (F_1 and F_2) as a result of the additional delocalisation of the π-electrons of the phenyl group associated with the conjugation effect.[14,35]

However, in certain chemical reactions of TFS conjugation is only weakly manifested. For example, the chlorination and bromination of $C_6H_5CF = CF_2$ afford $C_6H_5CFCl-CF_2Cl$ and $C_6H_5CFBr-CF_2Br$ respectively in 94–95% yields, i.e. the main process involves the ethylenic double bond, as for similar non-aromatic derivatives.[38]

αβ-Difluorostilbenes and their derivatives, which are obtained simultaneously with TFS and its derivatives in the synthesis via organolithium compounds, are also non-coplanar. The non-coplanarity of the structures of these compounds has been demonstrated by UV and ^{19}F NMR spectra; despite this, the conjugation effect does occur in molecules of this kind.[39]

3. Dimerisation of αββ-trifluorostyrene

Fluoroalkenes are known to exhibit a characteristic behaviour in polycentre reactions and, in contrast to the non-fluorinated monomers, they readily dimerise or react with other olefinic compounds, forming cyclobutanes by 1,2-addition.[40] The polarisation of the double bond does not affect their cyclodimerisation, which rules out an ionic mechanism. It has been suggested that the 1,2-addition reactions proceed via a two-step radical mechanism. A biradical, in which rotation about the C(1)–C(2) bond is possible, arises in the first stage:[40]



The coupling of fluoroalkenes in the first stage of the reaction proceeds in such a way that a radical centred on the carbon atom linked to the smallest number of fluorine atoms is produced. The "head to head" cyclodimerisation is not stereospecific and in the case of asymmetric fluoroalkenes leads to the formation of *cis*- and *trans*-isomers.

The tendency of TFS towards dimerisation is extremely pronounced. In all the early studies on the synthesis and polymerisation of TFS, it was already stated that this monomer readily dimerises.[3,24] Subsequently the dimerisation reaction and the dimer itself were investigated in fair detail.[29,41–48]

It is now regarded as generally recognised that TFS dimerises via a biradical two-step mechanism, illustrated schematically above. It has also been confirmed that this reaction is not stereospecific—the dimer is always formed as a mixture of *cis*- and *trans*-isomers. Their amounts in the mixture depend little on the process conditions and can be approximately equal.[29,42,48–51] In order to identify and establish the structures of these products, different methods have been used: spectroscopic, ^{19}F NMR, mass-spectrometric, chromatographic, etc. The results have been unambiguous.

From an analysis of NMR spectra, it has been suggested in recent years that the transition state in the dimerisation of TFS has symmetrical polarity and that the double bonds are polarised. A linear relation has been obtained between the Hammett constant σ and the ^{14}F NMR parameters and it has been suggested that the deformation of the π-electron clouds is caused by mutual repulsion and polarity.[41,46,47]

It has been demonstrated that heating of TFS in bulk or in hydrocarbon solvents in the absence of material initiators leads to the formation of dimeric products alone[29] and that this process is a second-order reaction: $V_{dim} = K_{dim}[M]^2$.[25,26,29] A relation has been derived for the determination of the dimerisation rate constant, which is $K = 1.5 \times 10^7 e^{-17652/RT}$.[49]

Table 3. The rate of dimerisation of TFS in bulk and in different solvents at 50 °C.[29]

System	TFS concentration, M	V_{dim}^*, % h^{-1}
In bulk (pH 6.0)	7.88	0.62
In bulk (pH 1.0)	7.88	0.64
Triethylamine (0.63 M)	7.28	0.66
Diethyl ether (0.22 M)	7.60	0.60
p-Benzoquinone (0.001 M)	7.60	0.65
In solution in cumene	3.06	0.72
In solution in toluene	2.84	0.76
In solution in toluene	6.27	0.70

*V_{dim} is the rate of dimerisation (adjusted to the TFS concentration in bulk).

The dimer is a mixture of a colourless oily liquid with a crystalline phase (the *trans*-isomer). The dimer completely freed from the monomer has no smell. On heating, one isomeric form of the dimer is converted into the other (*cis*–*trans* interconversion).

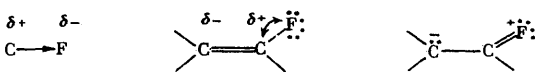
The dimer is extremely stable chemically but above 250 °C it decomposes back to the monomer: T_b = 120–121 °C at 6 mmHg, n_D^{20} = 1.4973;[3] n_D^{20} = 1.4954, d_4^{20} = 1.3884.[24] The rate of dimerisation of TFS depends only temperature[52] and the process is not inhibited or accelerated in the presence of various additives. Table 3 presents some results for the dimerisation of TFS in different systems.

III. Polytrifluorostyrene and αββ-trifluorostyrene copolymers

1. Polymerisation of αββ-trifluorostyrene

The presence of fluorine atoms in the TFS molecule leads to the specific behaviour of this monomer in polymerisation processes. We shall consider the causes of this behaviour.

The introduction of fluorine (the most electronegative element) atoms as substituents into the molecule of a saturated organic compound (at a carbon atom in the sp^3-state) usually leads to the appearance of a negative inductive effect ($-I_{eff}$). If the fluorine atom is linked to an sp^2-carbon atom of an unsaturated π-electron system, it exhibits the opposite effect, consisting in the repulsion of the π-electrons ($+I_{eff}$), which is due to the presence of three unshared electron pairs in the outer shell of the fluorine atom. A strong repulsion arises between the pairs of 2p electrons of the fluorine atoms and the pairs of $2p_\pi$ electrons at a neighbouring carbon atom. This effect, associated with the extremely strong influence on the reactivity of fluorine-containing monomers, is usually referred to as the "resonance-donor effect" or the R effect:[53]



$-I$ effect $+I$ effect $+R$ effect.

As a consequence of the $-I$ effect, the electronegative fluorine atom generates on the neighbouring carbon atoms an excess positive charge δ+. The pair of π electrons is then subject to the field of the positively charged carbon atoms which increases the Coulombic interaction of the π-electrons with the nuclei of these atoms. This alters their energy state and the symmetry of the distribution of electron density. As a result of this, the deformed cloud of π electrons becomes more extended along the C=C axis, binding more strongly the carbon nuclei.

For fluorinated styrenes, the change in the distribution of electron density on the C=C bond also entails a significant decrease in the conjugation of the π-electron double bond with the π electrons of the benzene ring (20%). The IR and Raman spectra of a series of fluorinated styrenes in the region of the C=C bond stretching vibrations indicate a greater strength of this bond compared with styrene.[54] Analysis of data on the copolymerisation of TFS with other monomers[55–57] shows unambiguously that TFS is more reactive than styrene.

As a consequence of the non-coplanarity of the TFS molecule, which was discussed in detail above, the effect of the polar factor for this compound is dominant and is hardly distorted by the effect of the conjugation with the benzene ring. Therefore the decrease in the reactivity of β-substituted fluoro-monomers is apparently caused precisely by the polar effect of the substituents.

The low reactivity of the TFS molecule and also the presence of fluorine atoms in it introduce definite characteristic features into the polymerisation of this monomer. The attempts to obtain the polymer by the traditional radical polymerisation in bulk and in solution, made in a number of studies, did not lead to the desired results.[3,29,58–60] The main reaction product under such conditions is a dimer, which consists of a mixture of isomers of diphenylperfluorocyclobutane, and a small amount of a low-molecular-weight polymer (oligomeric products with molecular weights in the range 1500–2000).[29] In such systems, the polymerisation of TFS involves the occurrence of two parallel and independent processes: dimerisation and oligomerisation.[29] The activation energy for the first process is then 58.58 kJ mol^{-1} and that for the second is 79.5–87.8 kJ mol^{-1} depending on the type of initiation.[29,52] When the process is carried out in solution, an increase in the dielectric constant of the medium leads to an increase in the molecular weight of the oligomer. Table 4 presents certain results for the polymerisation of TFS in different solvents.

Table 4. The rates of oligomerisation (V) of TFS in different solvents at 50 °C (AIBN*, 0.076 M).[29]

Solvent	ε	TFS concentration, M	$10^4 V$, mol litre^{-1} min^{-1}		Molecular weight
			Experimental	adjusted to concentration in bulk**	
In bulk	—	7.88	2.30	2.30	1 200
Cumene	2.23	3.06	0.94	2.42	1 100
Toluene	2.23	2.84	0.92	2.54	1 200
Toluene	2.23	6.27	2.23	2.27	1 170
Ethyl methyl ketone	18.0	4.88	3.36	5.26	2 000
N-Methylpyrrolidinone	31.0	3.14	2.02	5.05	4 300
Dimethylformamide	36.7	5.07	4.78	7.45	7 200
Sulpholan	44.0	4.23	10.72	20.17	10 000
Dimethyl sulphoxide	48.0	2.45	3.11	9.95	9 700

*AIBN = azobisisobutyrodinitrile—the initiator.
**The rate adjusted to the concentration in bulk on the assumption of a linear dependence of the rate of oligomerisation on the TFS concentration.

Nor can the high-molecular-weight polymer be obtained in an appreciable yield on polymerisation via ionic and ionic-coordination mechanisms in the presence of BF_3, $SnCl_4$, and Ziegler–Natta catalysts.[24,49,55,59,67]

A high-molecular-weight PTFS can be obtained only by emulsion polymerisation, which was first achieved by Prober in 1953.[3] The method of emulsion polymerisation still remains the only procedure for the synthesis of PTFS with a fairly high molecular weight and a high degree of conversion. Studies in this field can be divided into two groups: the study of the kinetics of the emulsion polymerisation of TFS in order to create a basis for the specific synthesis of PTFS[4,29,62,63] and the synthesis of PTFS with a specified set of properties.[3,24,55,59,60,64]

The first studies in this field already showed that the yield of the polymer and its molecular weight are affected to an appreciable extent by the nature of the emulsifying agent and its concentration

(the ratio of the phases comprising the aqueous solution of the emulsifying agent and the monomer) and also by the initiating system.[3,24,55,59] More detailed studies showed that a change (increase) in the rate of polymerisation and especially in the molecular weight on passing from the polymerisation of TFS in bulk to its polymerisation in emulsion has no analogues among other vinyl monomers. Thus for TFS the rate increases under these conditions by approximately a factor of 30 and the molecular weight increases by three orders of magnitude. Table 5 presents for comparison the corresponding data.[52] The polymerisation rate constant, activation energies, and pre-exponential factors for TFS and its *p*-methyl derivative using different polymerisation procedures were determined from the kinetic data. The data are presented in Table 6.[64] The ratio of the chain propagation and termination rate constants (k_p/k_t) for styrene proved to be greater by a factor of 4 than for TFS, while the chain propagation rate constant for styrene is greater by a factor of 400 than the value for TFS.

Table 5. Polymerisation of TFS under different conditions (0.5% BP relative to weight of monomer, 50 °C).[52]

Polymerisation conditions	Conversion, %	$10^3 V$, min^{-1}	M_n (ebullioscopic)
In bulk	12.0	2.1	1236
In bulk + 3.0 wt.% E-30	10.9	2.1	1200
TFS + water (phase ratio 1:7)	12.0	2.2	930
TFS in emulsion (phase ratio 1:7, 3.0 wt.% E-30)	24.0	63.0	$9 \cdot 10^{6}$*

*The molecular weight was determined by the light scattering method.

Table 6. Kinetic characteristics of the polymerisation of fluorostyrenes and their comparison with data for styrene.[64]

Polymerisation conditions, monomer	k_{60}, s^{-1}	E, kJ mol^{-1}	A, litre $mol^{1/2}$ $s^{1/2}$
TFS (in emulsion)	$4 \cdot 10^{-6}$	82.4	$3.5 \cdot 10^{7}$
p-Methyl-αββ-trifluorostyrene (in solution)	$0.9 \cdot 10^{-6}$	85.8	$2.6 \cdot 10^{7}$
p-Methyl-αββ-trifluorostyrene (in emulsion)	$2.6 \cdot 10^{-6}$	100.4	$1.3 \cdot 10^{9}$
Styrene (in solution)	$3.2 \cdot 10^{-6}$	88.7	$3.7 \cdot 10^{9}$
Styrene (in emulsion)	$16.0 \cdot 10^{-4}$	94.5	$6.0 \cdot 10^{11}$

However, one should note that the complete removal of HF from the reaction mixture makes it possible to obtain in bulk a polymer with a molecular weight of 30000 – 50000 at a system pH of 7.[29]

One of the distinctive features of the emulsion polymerisation of TFS is the marked dependence of the rate of the process and of the molecular weight of the polymer on the topochemistry of the initiation process. It has been established that only water-soluble initiators (of the type of persulphates) or oxidation-reduction systems whose components are soluble in different phases are capable of ensuring the maximum rates of reaction and the maximum molecular weights of the polymers obtained.[29,52,60,62,65]

Detailed study of the emulsion polymerisation of TFS made it possible to develop effective methods for the synthesis of this polymer in a form suitable for practical purposes.[29,52,62,65] It is noteworthy that TFS polymerises only when hydrocarbon emulsifying agents are used and that the best results are obtained in the presence of anionic emulsifying agents of the type of E-30 (sodium salt of $C_{15}-C_{16}$ alkanesulphonates) and their mixtures with non-ionic emulsifying agents of the type of hydroxyethylated alcohols.[29,52,60,62,65] The attempts to use for emulsion polymerisation of TFS fluorinated emulsifying agents—the salts of fluorocarboxylic acids which are widely employed in the polymerisation of many fluorine-containing monomers, did not yield positive results in the given instance.[66]

The emulsion system also affords fully cross-linked polymers when TFS is polymerised in the presence of polymeric peroxides.[63]

The attempt to obtain a high-molecular-weight PTFS in a high yield not in an emulsion system but by carrying out the process at a high pressure (up to 2000 MPa),[67] which likewise failed to give satisfactory results, should also be noted.

2. Physicochemical properties of PTFS and its structure

The PTFS obtained by emulsion polymerisation is a white powder (d_4^{20} = 1.4903 g cm^{-3}) readily soluble in organic solvents—benzene, diethyl ether, acetone, ethyl methyl ketone, tetrahydrofuran, ethylene chloride, etc.—and also in aprotic solvents. Transparent films can be obtained from solutions, their strength amounting to 100 MPa but their relative elongation does not then exceed several per cent. The brittleness of the films greatly limits the application of this polymer, although its high thermal and chemical stability combined with its ability to undergo modification by the introduction of various groups into the phenyl units makes this polymer extremely promising for the preparation of functional polymeric materials. PTFS is an amorphous polymer, but the X-ray diffraction pattern of an extended specimen reveals a weak tendency towards texture formation. The reflections corresponding to 2.35 and 4.66 Å are concentrated along the meridian. Such a picture for an extended specimen indicates a definite degree of orientation but does not confirm the presence of a crystalline phase. The orientation of the extended specimens is also demonstrated by the high degree of double refraction in crossed polarisers.[24]

It has been suggested that the PTFS molecules have the form of a distorted C–C–C zig-zag. The attempt to construct a model on the basis of this hypothesis demonstrated that, as a consequence of steric hindrance, isotactic disposition of the benzene rings is impossible. The molecule can exist only in the syndiotactic version.[29] The NMR study of the structure of the *p*-methyl-αββ-trifluorostyrene homopolymer showed, however, the presence of non-equivalent CF groups of three types, which it has been suggested refer to the isotactic, syndiotactic, and heterotactic sections of the polymer chain.[68]

It has also been established that vitreous PTFS has different mechanical properties depending on the formation conditions of the specimens (from the melt or from solution), similarly to what has been observed for crystalline polymers.[69] It has been noted that certain important properties of the polymers (for example, their brittleness) depend on the supermolecular structure formation which

develops very slowly. This plays an especially notable role for the sulphonated PTFS, in which the formation of structural elements leads to an appreciable improvement of the strength characteristics but develops extremely slowly. The introduction of small amounts (up to 4%) of certain low-molecular-weight additives (for example, dibutyl phthalate) greatly accelerates the structure formation and leads to the strengthening of the polymer.[69] A change in the structure occurs also at low temperatures (in the range 4.2–300 K and for 1–2 Hz).[70]

Light scattering and viscometric studies of PTFS solutions showed that this polymer has chains with an enhanced rigidity and occupies an intermediate position between flexible chain and rigid chain polymers.[71] The increased skeletal rigidity of the PTFS chains is probably induced by the appreciable retardation of the internal rotation caused both by the increasing steric hindrance to their rotation owing to the large van der Waals radius of fluorine and by the dipole–dipole interaction of the polar C–F bonds. It is noteworthy that the comparatively high rigidity of the PTFS molecules (greater by a factor of four than that of styrene) is not caused by a secondary structure but is due to the true skeletal rigidity of its single-stranded chain.[29]

PTFS is an infusible polymer and cannot be worked in the molten state. Certain data on the softening temperature as well as the dielectric characteristics of PTFS films are presented in Table 2. PTFS has low dielectric losses over a wide frequency range[24] and some of its copolymers are polymeric dielectrics with an enhanced thermal stability.[72] However, the thermal stability of PTFS is appreciably lower than that of polytetrafluoroethylene (PTFE),[73] although in terms of its decomposition products (the yield of the pure monomer) PTFS is closest to PTFE. Thus the yield of the pure monomer on thermal degradation of PTFE, PTFS, poly(chlorotrifluoroethylene), poly(trifluoroethylene), poly(vinyl fluoride), and poly(vinylidene fluoride) is respectively M > 95, 75, 28, <1, <1.[74] According to mass-spectrometric data, the content of the monomer in the degradation products is 73.6%, while 26.4% corresponds to heavy fragments with an average molecular weight of 458.

On irradiation of PTFS with ^{60}Co γ-rays at a dose of 10^{22} eV g^{-1}, the radiation-chemical yield $G_{\text{cross-link}}$ does not exceed one, which indicates an appreciable radiation stability of the polymer, similar to that of the usual styrene.[75]

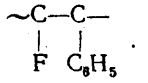
During recent decades, TFS together with other monomers and compounds which are difficult to polymerise has been polymerised in plasma. Films with improved thermal stability and containing oxygen were obtained on its surface.[76,77] The rate of formation of polymer films in a discharge plasma is 54 Å s^{-1} for TFS against 132 Å s^{-1} for styrene.[77]

3. Copolymerisation of αββ-trifluorostyrene

As already mentioned, the introduction of fluorine atoms into the vinyl group of styrene leads to specific features in the polymerisation of TFS. The copolymerisation reaction of this monomer is of interest from the standpoint of the effect of the fluorine atoms on the reactivity of TFS. It too constitutes a method of synthesis of new polymeric materials based on it and is a procedure for the modification of PTFS.

Data on the radical copolymerisation of fluorostyrenes confirm that the effect of fluorine atoms on the conjugation energy in these compounds is low. Systematic studies on the effect of the location of fluorine atoms on the reactivity of these monomers have made it possible to arrange fluorostyrenes in terms of their increasing reactivity in the following sequence:[57] ββ-difluorostyrene < β-fluorostyrene < αβ-difluorostyrene < TFS < pentafluorostyrene < 2,4-difluorostyrene < *p*-fluorostyrene.

The decrease in the reactivity of β-substituted fluoro-monomers can be attributed only to the polar effect of the substituents, since the effect of fluorine on the conjugation energy in the monomer is very insignificant and may be neglected. Being an electron acceptor, the fluorine in the β-position diminishes the electron density on the double bond and the monomer plays the role of an electron-donating partner in copolymerisation reactions. However, the decrease in the reactivity of the monomer is not compensated, as for the α-substituted monomers, by the increase in the reactivity of the radical, because the substituent in the radical formed is separated from the radical centre by the aliphatic C–C chain:[57]



As a result of all these factors, the constant for the copolymerisation of β-substituted styrenes [M_2] is low or even zero.

Table 7 illustrates the effect of the β-substitution of fluorine atoms on the parameters of the copolymerisation of styrene with fluorostyrenes. Thus, in the copolymerisation of styrene with *p*-fluorostyrene, the copolymerisation constants are very similar for both monomers, which is evidently caused by the weak inductive effect of the fluorine in the aromatic ring on the double bond. In the case of the styrene–2,4-difluorostyrene pair, there is some enrichment of the copolymer in styrene. The conjugation in the molecule of 2,4-difluorostyrene partly compensates for the polar effect of the fluorine atoms and the constants therefore differ insignificantly. Pentafluorostyrene enters into the polymer chain much less effectively. This is apparently caused by the steric hindrance due to the presence of the cumbersome perfluorovinyl groups and/or the effect of the polar factor.

Table 7. Copolymerisation of styrene with fluorinated styrenes.[57]

Monomer	r_1	r_2	Q	e
p-Fluorostyrene	0.7	0.9	0.83	−0.12
2,4-Difluorostyrene	1.05	0.75	0.65	−0.32
Pentafluorostyrene	1.53	0.62	0.22	0.52
β-Fluorostyrene	5.96	0.01	0	—
ββ-Difluorostyrene	10.4	0	0	—
αβ-Difluorostyrene	2.44	0.04	0.1	0.94
TFS	3.5	0.15	0.15	—

Remarks. r_1 and r_2 are copolymerisation constants, Q is a quantity characterising the reactivity of the monomer, and e is the polar factor.

In the case of β-fluorostyrene, the reactivity of the monomer diminishes very greatly. This is a result of the polar effect of the fluorine atom and not of steric hindrance. In the copolymerisation of ββ-difluorostyrene, the polar effect is manifested even more sharply and the homopolymerisation of styrene actually takes place.

The introduction of a fluorine atom into the α-position in β-fluorostyrene activates the monomer. Thus αβ-difluorostyrene and TFS are more reactive in copolymerisation than ββ-difluorostyrene or β-fluorostyrene.[55]

Table 7 presents quantities characterising the copolymerisation of styrene with these fluorine-containing compounds.[57] Attempts to obtain copolymers of TFS with other monomers containing, and not containing, fluorine atoms have been made since the 1950s. The aims of these studies were various. The task in most of them was the synthesis of new chain materials with improved thermal and chemical stabilities, modification (improvement of physicomechanical properties of PTFS), and the introduction of functional groups into the copolymers in order to obtain mainly ion-exchange materials. Quite a few studies have also been devoted to theoretical aspects of problems of the reactivity of the monomers, as already pointed out.

The copolymerisation reactions of TFS with styrene, its derivatives, and methyl methacrylate under various conditions have been studied in greatest detail.[24,29,55,56–72,78–85] The properties of the copolymers and their molecular weights were varied within wide limits, which determined to a large extent the properties of the materials obtained. Table 8 presents certain data for such copolymers.[78]

Table 8. Copolymerisation of αββ-trifluorostyrene and its derivatives.[78]

Copolymer	Copolymerisation time, h	Yield of copolymer, %	Composition of copolymer, mol%		[η]* (in benzene)
			M_1	M_2	
TFS [M_1]–styrene [M_2]	8	74	28.53	71.47	2.7
	7	70	39.77	60.23	2.8
	8	60	48.53	51.47	1.8
	8	40	53.75	46.24	0.9
TFS [M_1]–2,5-dimethylstyrene [M_2]	4	90	50.53	49.17	1.1
	4	50	60.77	39.23	0.6
TFS [M_1]–methyl methacrylate [M_2]	6	—	43.29	56.71	0.4
	11	41	53.88	46.22	0.2
m-Methyl-αββ-TFS [M_1]–styrene [M_2]	2.5	40	46.27	53.73	0.5
o-Methyl-αββ-TFS [M_1]–styrene [M_2]	33	11	50.41	49.59	0.5
p-Methyl-αββ-TFS [M_1]–styrene [M_2]	7	55	46.97	53.03	2.0
	7	64	36.77	63.23	1.4

*[η] is the intrinsic viscosity measured in benzene.

Comparison of the thermal stabilities of different copolymers of TFS with styrene and its derivatives showed that the highest thermal stability (190 °C) is exhibited by TFS–2,5-dimethylstyrene copolymers.[72,79] Certain other characteristics of copolymers based on TFS have also been determined.[79,86]

Attempts have likewise been made to obtain ternary TFS–styrene–diene copolymers.[82,84,85,87,88]

Among other monomers which copolymerise with TFS and its derivatives, the greatest interest attaches to monomers based on acrylic and methacrylic acids and their derivatives.[78,88–94]

The copolymerisation of TFS with divinylbenzene, leading to the formation of cross-linked insoluble polymers, has been carried out mainly in order to obtain on subsequent sulphonation ion-exchange materials with improved thermal and chemical stabilities.[88,95–99] This is described in greater detail below.

The attempt to obtain a peroxide oligomer by the copolymerisation of TFS with a redox initiating system containing diene or vinyl units is also noteworthy. Such oligomers are used to vulcanise rubbers in order to obtain chemically stable vulcanised materials.[100]

Among all the possible TFS copolymers, its copolymer with tetrafluoroethylene would be of greatest interest. Such a copolymer would possess unique properties—high chemical and thermal stabilities since it would have a fully fluorinated main chain, effective physicomechanical properties as a result of the introduction of flexible TFE units, and the ability to dissolve owing to the presence of phenyl groups. However, it is extremely difficult to achieve such copolymerisation for a number of reasons, although in principle, it should be possible. Hitherto, there have been only isolated mentions of the synthesis of such copolymers.[101,102] The copolymer is obtained, for example, by emulsion polymerisation with radical initiation in the presence of dodecylamine hydrochloride or sodium lauryl sulphate in an autoclave. Table 9 presents the characteristics of this copolymer obtained by the emulsion method.[102]

As can be seen from the results in Table 9, the rate of copolymerisation of TFS with TFE and the yield of the copolymers are extremely low. Depending on the composition of the initial mixtures and the excess of TFE, their content of TFE:TFS units can vary from 2:95 mol% to 95:5 mol%. The copolymers obtained have low molecular weights, are soluble, and form fairly satisfactory films.

IV. Ion-exchange materials based on polytrifluorostyrene. Their synthesis and properties

The presence in each monomer unit of PTFS of a benzene ring makes possible the introduction into the latter of different functional groups with retention of the main perfluorinated chain. The introduction of ionogenic groups (sulphonic and carboxylic acid groups, phosphorus-containing groups, amino-groups, and certain others), which lead to the formation of valuable ion-exchange materials with improved resistance to corrosive influences, is most promising in this respect. The commonest method for the introduction of such groups is sulphonation of PTFS, which affords ion-exchange materials with good electrochemical characteristics.

1. Homogeneous cation-exchange membranes

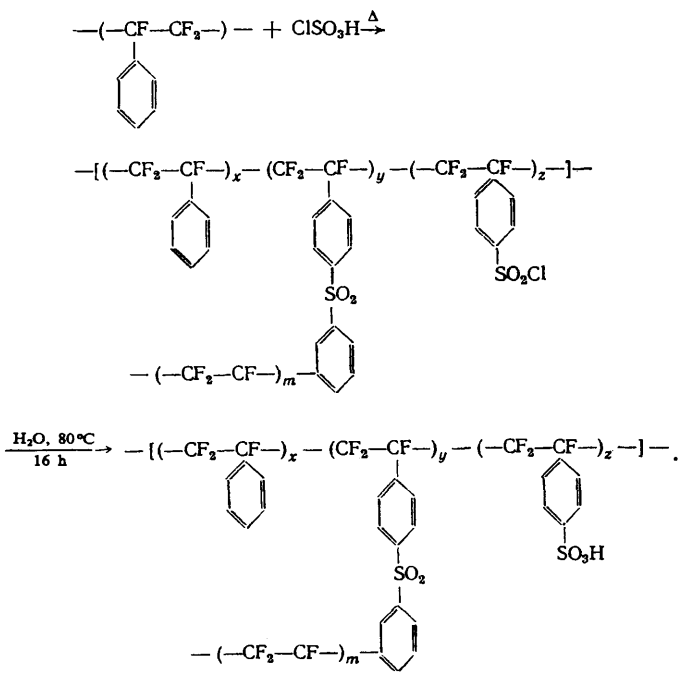
Numerous studies have been devoted to the sulphonation of PTFS in order to obtain cation-exchange materials with improved resistance to the action of corrosive media.[59,103–112] The sulphonation is usually carried out with chlorosulphonic acid or SO_3 in a dry halogen-containing solvent (usually chloroform) in the presence of an excess of the sulphonating agent. This results in the

Table 9. Copolymerisation of αββ-trifluorostyrene with tetrafluoroethylene.[102]

Recipe and copolymerisation conditions	Composition of copolymer, TFS:TFE, %	Characteristics of copolymer			
		viscosity [η]	T_g, °C	T_{decomp}, °C	elemental composition, %
TFS—16 g TFE—11.5 g $(NH_4)_2S_2O_8$—0.1 g $NaHSO_3$—0.05 g $C_{12}H_{25}NH_2.HCl$—1.45 g Water—50 ml Temperature—40 °C Duration—24 h Yield—2.2 g	90.7:9.3	0.35 dl g^{-1} [determined at 35 °C in ethyl methyl ketone (EMK)]	186 (Perkin–Elmer differential calorimeter)	361 (onset weight loss)	F—39.65 C—58.52 H—3.13
TFS—16 g TFE—250 g $FeSO_4.7H_2O$—2.4 g 50 ml of 3% H_2O_2 Ascorbic acid—12 g Water—500 ml Temperature—0–5 °C Duration—24 h Yield—3 g	64:36	0.15 dl g^{-1} (determined at 35 °C in EMK)	—	—	F—46.1 C—51.3 H—2.05

Remarks. The copolymers obtained are soluble in acetone, from solutions in which transparent flexible films can be cast.

formation of a polymer with different degrees of sulphonation and having both linear and cross-linked structures.



Depending on the sulphonation conditions and the presence of an excess of the sulphonating agent, the ratio of the linear and cross-linked sulphonated PTFS can be various.

There also exists a method for the synthesis of PTFS which is fully linear with a controllable number of sulpho-groups and which is in addition soluble in different solvents. The method reduces to sulphonation in solution with constant removal of the solvent whilst maintaining a constant concentration of the sulphonating agent.[113] In this way, it is possible to obtain sulphonated PTFS ranging from a water-soluble polymer [in the presence of a high content of sulphur-groups (>30 mol%)] to a polymer soluble in different hydrocarbon solvents (when the content of sulphur-groups is <10 mol%) and which can be worked in such solvents. The films obtained from the sulphonated PTFS can be used as ion-exchange membranes with high exchange capacity (>1 mequiv./g of polymer) and a low specific resistance. However, such films have low strength characteristics and are very brittle in the dry state.

Table 10 presents the sulphonation conditions (concentration of the sulphonating agent, its excess, and reaction time and temperature) and the characteristics of homogeneous ion-exchange membranes based on sulphonated PTFS for a large number of specimens sulphonated to different extents.[103] It follows from the analysis of the data presented that a low concentration of the sulphonating agent (<0.1 M) and a ratio of the sulphonating agent and the phenyl groups below the stoichiometric value ensure the formation of a non-cross-linked sulphonated PTFS with a fairly high degree of sulphonation (up to the presence of a sulpho-group in each benzene ring) and an exchange capacity >1. With increase in the concentration of the sulphonating agent to a value close to 1 M and above and when its excess relative to the phenyl groups is by a factor of several units, the sulphonation process affords a cross-linked product insoluble in all solvents and characterised by an approximately uniform exchange capacity (Table 10). This shows that it is undesirable to increase the excess of the sulphonating agent, although this permits a reduction of the process temperature. It

Table 10. Preparation and properties of sulphonated polytrifluorostyrene and homogeneous ion-exchange membranes based on it (PTFS with a molecular weight of 125000 was used).[103]

Preparation and properties	1	2	3	4	5	6	7	8	9	10	11	12
Sulphonating agent, molar concentration	0.021	0.048	0.096	0.021	0.04	0.86	1.42	1.0	1.0	1.0	0.85	1.14
Reaction time, h	3	3	3	3	3	4	4	4	4	4	12	4
Temperature, °C	60	60	60	50	60	30	30	40	50	60	30	30
Sulphonating agent: phenyl groups molar ratio	0.2	0.45	0.92	0.2	0.25	8.2	14.1	9.8	9.8	9.8	8.2	11.1
Gravimetric exchange capacity, mequiv/g of polymer	1.23	1.98	4.07	0.95	0.87	2.05	2.11	2.46	2.92	3.35	2.15	2.28
Solubility:												
Methanol	+	+	+	+	+	—	—	—	—	—	—	—
Ethanol	+	+	+	+	+	—	—	—	—	—	—	—
Isopropyl alcohol	+	+	—	+	+	—	—	—	—	—	—	—
Butanol	+	+	—	+	+	—	—	—	—	—	—	—
Acetone	+	+	+	+	+	—	—	—	—	—	—	—
Formamide	+	+	—	+	+	—	—	—	—	—	—	—
Dimethylformamide	+	+	—	+	+	—	—	—	—	—	—	—
Dioxan	+	+	—	+	+	—	—	—	—	—	—	—
Benzene, chloroform, hexane	—	—	—	—	—	—	—	—	—	—	—	—
Water	*	*	+	*	*	*	*	*	*	*	*	*

*Insoluble in water but swells.

Table 11. Properties of heterogeneous membranes based on sulphonated polytrifluorostyrene and a second polymer without ionogenic groups in its composition.[103]

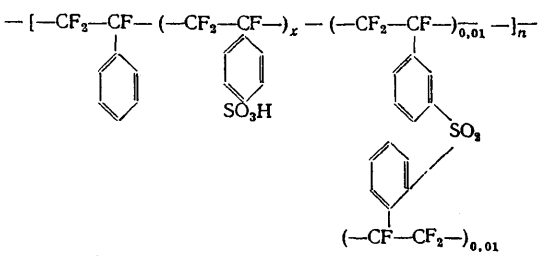
Characteristics and type of polymer	1	2	3	4	5	6	7	8	9	10	11	12
Gravimetric exchange capacity, mequiv/g of polymer	0.8	0.9	1.2	0.9	0.6	0.85	1.33	0.7	0.79	0.4	0.9	0.73
Resistance:												
H^+, Ω cm	28	42	—	—	—	25	18.5	21.9	13	—	—	70
K^+, Ω cm	—	3.01	23	—	5.54	—	—	—	—	7.0	4.2	—
Ion-exchange polymer, wt.%	20	50	67	50	67	35	50	30	33	50	50	50
Type of inert polymer, wt.%												
Kynar	80	50	33	—	—	—	35	—	—	—	—	—
Viton A-HV	—	—	—	50	33	—	—	—	—	—	—	—
CTFE–VF copolymer	—	—	—	—	—	65	15	—	—	—	—	—
Kel-F 810	—	—	—	—	—	—	—	70	—	—	—	—
Chlorosulphonated polystyrene	—	—	—	—	—	—	—	—	67	—	—	—
Poly(vinyl chloride)	—	—	—	—	—	—	—	—	—	50	—	—
Poly(vinylidene chloride)	—	—	—	—	—	—	—	—	—	—	50	—
Butadiene–styrene copolymer	—	—	—	—	—	—	—	—	—	—	—	50

follows from the data presented that all the parameters affect to some extent the characteristics of the sulphonated PTFS and hence the method of synthesis of ion-exchange materials from it.

2. Heterogeneous cation-exchange membranes

Heterogeneous membranes with good electrochemical parameters and better, compared with homogeneous membranes, physicochemical characteristics are also obtained from sulphonated PTFS. Such membranes are prepared either by mixing solutions of the corresponding polymers or by blending solid powdered polymers

with subsequent manufacture of the membranes from them.[103] These membranes are characterised by lower exchange capacities compared with the homogeneous membranes as a consequence of their appreciable content of an inert polymer but are more promising both in view of their improved physicomechanical properties and by virtue of the possibility of using different inert polymers depending on the operating conditions. Blends of polymers can also be used as neutral components of membranes of this kind; in such cases the heterogeneous membranes are obtained by blending three and more polymers.[104] The ionogenic component in the heterogeneous membranes is cross-linked sulphonated PTFS having the following structure:



$x = 2.3$.

Table 11 presents examples of different compositions of heterogeneous membranes and some of their electrochemical characteristics.[103]

Table 12. Surface modification of heterogeneous ion-exchange membranes based on sulphonated PTFS.[110]

Solutions of reactants (parts by weight)	Reaction conditions		ρ, Ω cm²	Transport number	Current yield, %	Concentration of NaCl in 5 M NaOH, M
	T, °C	time, h				
Naphthalene (30) $AlCl_3$ (10) CS_2 (60)	30	16	6.2	0.87	92	0.002
Xylene (30) $TiCl_4$ (10) CCl_4 (60)	30	8	6.3	0.87	91	0.004
Fluorene (20) $SnCl_4$ (5) CCl_4 (75)	30	16	6.2	0.87	90	0.005
Benzene (40) $AlCl_3$ (15) CCl_4 (45)	30	8	6.5	0.87	91	0.003
Without treatment	—	—	6.0	0.84	77	0.03

Like the best ion-exchange membranes available at present, which are based on a material of the Nafion type, the homogeneous and heterogeneous ion-exchange membranes obtained from sulphonated PTFS are designed for use under severe conditions (mainly in chlorine electrolysis in electrolytic cells). In terms of their electrochemical properties, these membranes are indistinguishable or differ little from the corresponding membranes based on the Nafion type material but are appreciably inferior to them as regards mechanical properties.

In order to improve certain electrochemical parameters, such membranes are subjected to surface modification which can be readily carried out using the Friedel–Crafts reaction by introducing various groups into the benzene rings of PTFS. Table 12 presents the changes in the current yield and in the selectivity of the membranes obtained by blending 30 parts by weight of the sulphonated and cross-linked PTFS with 70 parts by weight of a fine poly(vinylidene fluoride) powder (Kynar) using a blending and pressing procedure.[110]

3. Grafted cation-exchange membranes prepared using sulphonated polytrifluorostyrene

Membranes based on sulphonated PTFS, which have good thermal and chemical stabilities, are particularly valuable ion-exchange materials which are resistant to corrosive influences. However, such membranes, especially homogeneous ones, are characterised by inferior physiochemical parameters compared with membranes of the Nafion type. One of the most promising procedures for overcoming these disadvantages proved to be the grafting of TFS onto different films (usually fluorine-containing polymers) with subsequent sulphonation of the resulting graft copolymers or by introducing other ionogenic groups into their benzene rings.[99,101,114–125] The grafting is carried out as a rule by a radiation method.

Films made up of polyethylene, polytetrafluoroethylene, poly(chlorotrifluoroethylene), the ethylene–TFE copolymer, the propene–TFE copolymer, poly(chloroethylene), the hexafluoropropene–vinylidene fluoride copolymer, the heptafluoropropene–TFE copolymer, the copolymer of TFE and perfluorinated vinyl ethers (Nafion), and other materials are used as inert supports. The irradiation dose is 1–30 Mrad. The films are irradiated in air and in oxygen or inert media. This results in the formation of radicals whose lifetime in an inert atmosphere is up to two weeks at 0 °C, up to seven days at 10 °C, and 2–3 days at room temperature.[118,119] In order to obtain graft TFS polymers on different supports, the irradiated films are placed in TFS or its solutions in chloroform, tetrachloroethane, CCl_4, Freon 113, or benzene and are kept there at a temperature of 10–90 °C for 1–50 h. The degree of grafting is 10–50%. The characteristics of such membranes are quite good and are comparable with those of ion exchange membranes based on Nafion. Comparative data for ion-exchange membranes based on the ethylene–TFE copolymer on which TFS has been grafted with subsequent sulphonation and for Nafion 120 membranes[119] are presented below.

Membrane	Exchange capacity, mequiv g^{-1}	ρ, in 0.5 M KCl, Ω cm²	Extensibility	Transport number, 0.5 M KCl/1 M KCl
With grafted TFS	0.61	1.71	3.4—4.5	0.94
Based on Nafion	0.83	1.48	4.0	0.93

Such membranes can be used as diaphragms for any purposes (the electrolysis of water, NaCl, and the Glauber salt, low-temperature dialysis, etc.). The methods employed provide for the irradiation of only the initial films, while TFS is not irradiated. They are economical and readily applied. Table 13 presents the characteristics of certain cation-exchange membranes obtained by grafting TFS onto different 100 μm supports with subsequent sulphonation in the

course of 40 min with chlorosulphonic acid in CCl_4 or tetrachloroethylene at 40 and 135 °C respectively.[119]

Table 13. Cation-exchange membranes obtained from different polymers by the radiation grafting of TFS and subsequent sulphonation.[119]

Support	Degree of grafting, %	Degree of sulphonation, %	Characteristics of membrane			Resistance to action of oxidant (weight loss)
			exchange capacity, mequiv. g^{-1}	ρ, Ω cm^2	transport number, 0.5 M KCl/1 M KCl	
Polyethylene (low density)	23	95	1.5	1.4	0.9	15
Poly(vinylidene fluoride)	20	60	0.6	3.2	0.93	10
TFE–ethylene copolymer	21	90	1.0	—	—	3
TFE–ethylene copolymer	16	80	0.7	3.5	0.93	3
Polytetrafluoroethylene	—	—	—	4.0	0.93	1

*Treatment with 3% H_2O_2 containing 4 p.p.m. of Mohr's salt at 70 °C for 24 h.

There is also a radiation method for grafting TFS onto inert films by irradiating the latter in a solution of the monomer. In this case, the degree of grafting for identical doses is regulated by the TF concentration in solution in different solvents and depends on the nature of the latter. Table 14 present data for the grafting of TFS onto the TFE–hexafluoropropene (HFP) copolymer in different solvents.[115] TFS was grafted onto a film which was placed in the form of a roll into the corresponding TFS solution, the chamber was evacuated or filled with an inert gas, and the temperature was kept at a level such that the solvent did not evaporate.

Table 14. Degree of radiation grafting of TFS at a dose of 2.59 Mrad.[115]

TFS concentration, %	Benzene, %	Degree of grafting, %	TFS concentration, %	Methylene chloride, %	Degree of grafting, %
10	90	1.4	10	90	2.5
30	70	8.2	30	70	9.7
50	50	14.3	50	50	17.6
70	30	24.0	70	30	27.1

4. Anion-exchange and other membranes prepared using grafted αββ-trifluorostyrene

Films with grafted TFS can be used after the appropriate treatment not only as cation-exchange membranes with sulphonic and carboxylic acid or phosphorus-containing groups but also as anion-exchange membranes after appropriate amination or as neutral membranes.[119]

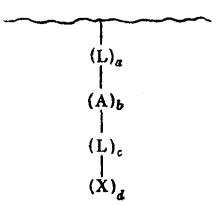
Anion-exchange membranes obtained by the radiation grafting of TFS onto different supports with subsequent chloromethylation and the preparation of quaternised aminated derivatives are of great interest. The reagents used for this purpose are CH_3OCH_2Cl, paraformaldehyde $(CH_2O)_3$, and HCl with which the grafted films are treated in the presence of $AlCl_3$ or $ZnCl_2$ as catalysts at 40 to 80 °C. The films are then treated with 5–50% aqueous solution of trimethylamine, triethylamine, or 2-hydroxyethyl(dimethyl)amine. Such anion-exchange membranes have good electrochemical parameters and an improved resistance to hydrolysis. The relevant data are presented in Table 15.[119]

Table 15. Anion-exchange membranes prepared from different polymers with radiation grafted TFS and subsequent chloromethylation and amination.[119]

Support	Degree of grafting, %	Degree of chloromethylation, %	Characteristics of membranes			Resistance to hydrolysis*
			exchange capacity, mequiv.g^{-1}	ρ, Ω cm^2	transport number, 0.5 M KCl/1 M KCl	
Polyethylene (low density)	23	80	0.86	4.2	0.92	without changes
Poly(vinylidene fluoride)	20	78	0.75	5.0	0.93	ditto
TFE–ethylene copolymer	18	80	0.70	4.8	0.94	»
Polytetrafluoroethylene	18	80	0.71	6.0	0.93	»

*Hydrolysis in distilled water at 95 °C for six days.

An interesting method of synthesising ion-exchange materials involves radiation cografting of a mixture of vinyl monomers and dicarboxylic acids onto a perfluorinated base. TFS can also be used as the vinyl monomer. Such ion-exchange materials can be represented schematically as the main perfluorinated chain with grafted side groups of the type[126]



where $a \geqslant 1$, $b \geqslant 0$, $c = 0.1$ or above, and $d \geqslant 1$, L represents the vinyl monomer residue, A represents active groups (dicarboxylic acids or their derivatives), and X is the polymer chain, capable of being terminated, or a fluorinated hydrocarbon polymer.

Insoluble cation-exchange resins with different exchange capacities have been obtained by copolymerising TFS with divinylbenzene and then sulphonated.[95,97,103,109]

V. Other aspects of the applications of polytrifluorostyrene

Together with the well known applications of PTFS as ion-exchange materials resistant to the action of corrosive media, this polymer is used for a number of other purposes. The use of PTFS for the preparation of an ultrafine fibrous filtering material FSPF (fluorostyrene Petryanov filter) proved to be the most promising application. This material is capable of withstanding repeated sterilisation with hot steam up to a temperature of 150 °C without change in filtration efficiency (99.99% with respect to an oil mist) and in physicomechanical parameters. The FSPF material is designed for use in bacterial filters sterilised by hot steam whose purpose is to free air from microorganisms in the microbiological, medical, and food industries and in health service establishments.[127–129]

Sulphonated PTFS can be employed as a catalyst in the synthesis of esters from neoalkylpolyols and aliphatic acids, its use greatly improving the properties of the products synthesised and simplifying their isolation from the reaction masses.[130] PTFS sulphonated to different extents can be used also in highly sensitive elements for a gravimetric hygrometer[131] and as a complex-forming material with a high selectivity in the separation of certain mixtures.[132]

The PTFS base material FC-430 is introduced in small amounts into compositions for the protection of films against electrochemical corrosion.[133]

PTFS-based materials with effective adhesion and antistatic properties are also employed to coat the grains of a photographic material.[134]

It has recently been reported that polymeric optical fibres, with excellent optical properties and a high capacity for the transmission of light have been prepared using PTFS.[135] PTFS is employed as their core. The losses in light transmission in such fibres are 130 dB km^{-1} (at 660 nm), 280 dB km^{-1} (at 780 nm), and 440 dB km^{-1} (at 850 nm).

PTFS has found recently an extremely interesting new application in the formation of negative electronic resistors with a high sensitivity, high chemical and thermal stabilities and a satisfactory resistance to dry etching.[136] In order to obtain such coatings, a solution of PTFS in chlorobenzene is deposited onto a silicon plate. On irradiation with a stream of fast electrons and subsequent treatment, coatings having a surface relief with a high resolving capacity, good adhesion, and a high resistance to dry etching are obtained.

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X-Ray diffraction studies on electron density in organic crystals

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ABSTRACT. The review presents the advances in precision X-ray diffraction studies on electron density in organic crystals carried out during the last several years. The methods for the elimination of and allowance for experimental errors, procedures used to interpret the results, and the characteristic features of the distributions of the deformation electron density in organic molecules are discussed.

The bibliography includes 126 references.

Contents

I. Introduction 592
II. Determination of the experimental distributions of ρ and δρ 592
III. Primary interpretation of electron density distributions 593
IV. Trends in the distributions of deformation electron density 599

I. Introduction

The spatial distribution of electron density $\rho(\mathbf{r})$ in a crystal was initially the principal result of X-ray diffraction analysis (XRDA). However, it was not until the middle of the 1960's that an increase in the experimental accuracy (automatic diffractometers), the correct allowance for systematic errors, the improvement of models (anisotropic thermal parameters), and the creation of special sets of programs made it possible to formulate the problem of the real physical significance of the asymmetry of the ρ maxima.

The first X-ray diffraction studies on organic crystals, whose authors claimed to have achieved an objective description of the details of the electron density distribution $\rho(\mathbf{r})$, were published in 1966–1967.[1–5] This was associated with the use in Fourier synthesis of thermal parameters obtained from neutron diffraction data or data on the large angle scattering of X-rays. Thus the effects of the non-sphericity of the distribution of valence electrons were successfully separated from the effects of thermal motion. The redistribution of electron density on formation of chemical bonds was represented by the deformation electron density $\delta\rho(\mathbf{r})$:

$$\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0(\mathbf{r}) = \sum_{\mathbf{q}} (F(\mathbf{q}) - \tilde{F}(\mathbf{q})) \exp(i\mathbf{rq}), \quad (1)$$

where ρ_0 is the electron density of the "precrystal" made up of spherically symmetrical non-interacting atoms, which are distributed and vibrate as in the crystal, $\mathbf{q}$ the radius-vector of the inverse lattice site, $\tilde{F}(\mathbf{q})$ the structural amplitudes of the "precrystal", and $F(\mathbf{q})$ the structural amplitudes of the crystal with the initial phases taken from $\tilde{F}(\mathbf{q})$.

Nevertheless, the procedures available to the investigators in the 1960's at best yielded a first aproximation to the solution of this fundamental problem. In subsequent years the improvement of various aspects of the method of determination of the functions ρ and δρ made it possible to achieve reproducible (similar in analogous cases) results: δρ maxima of reasonable size were usually observed in the internuclear space of chemically bound atoms and it was usually possible to detect also peaks corresponding to lone electron pairs (LEP) and to discover the characteristic features of the distribution of δρ in the regions of hydrogen bonds.

The outcome of the studies of the charge distributions in organic crystals during the period from 1966 to 1984 was summarised in a review.[6] In recent years, new steps of fundamental importance were taken in this research field. Here we have in mind (1) the improvement of the method of determination of experimental data, (2) progress in the interpretation of the distributions of ρ obtained, and (3) the accumulation of information about the distributions of δρ for a wide variety of chemical compounds, which makes it possible to discuss successfully detailed features of chemical bonds. The aim of the present review is a consistent discussion of these three aspects of the latest studies on precision XRDA of organic crystals. The main outcome of the research under consideration apparently consists in the fact that, whereas previously mainly qualitative aspects of the subject were investigated, it has now become possible to guarantee the quantitative reliability of the details of charge distributions discussed.

II. Determination of the experimental distributions of ρ and δρ

The characteristic features of the precision X-ray diffraction experiment, the principles governing the construction of the distributions of ρ and δρ, and also the errors of these distributions have been examined in a review.[7] Certain methods reducing the errors in the determination of experimental data and in their subsequent treatment and the latest examples of their application, demonstrating the great sensitivity of δρ maps to such correction, are presented below. The wide-scale use of the function δρ is due to two causes. Firstly, the difference between two convergent series (1) converges faster than either individual series and the termination of the series therefore affects δρ less than ρ. Secondly, the distribution of ρ requires some kind of procedure for primary interpretation[8] while the distribution of δρ is a result of one of the versions of such interpretation.

In order to obtain ρ, it is necessary in the first place to convert correctly the experimental intensities into the moduli of structural amplitudes, which involve the introduction of a series of corrections for systematic experimental errors.[7] These are for example, the

allowance for the anomalous and thermal diffuse scattering, extinction, and absorption.

Allowance for anomalous scattering is essential in the presence of heavy element atoms and is not usually carried out in their absence. Thus in the case of sulphur (thiourea) it causes little change in $\delta\rho$.[9] Allowance for thermal diffuse scattering is extremely important.[10] Without it, the thermal parameters of atoms proved to be too low (for example, by 12% in oxalic acid), but this is not reflected in the qualitative features of the distributions of $\delta\rho$ in the region of chemical bonds and lone pairs.[11]

The greatest difficulty arises in allowing for the extinction contribution. Although at the present time methods are available for such allowance, the introduction of the appropriate corrections for single crystals of different size and shape leads to appreciable differences in the heights and positions of the $\delta\rho$ maxima.[12] The intensity and small wavelength of synchrotron radiation make it possible to investigate single crystals whose diameter is less than 0.1 mm. The small size of the crystals diminishes the influence of extinction and absorption.[13] These and other advantages of synchrotron radiation (the possibility of reducing anomalous scattering by modifying the wavelength, the increased accuracy of the analysis of the peak profile by virtue of the small divergence of the beam) make its use in precision X-ray diffraction analysis extremely promising.

Appreciable changes in $\delta\rho$ maps (especially near the nuclei) occur even after small changes in the scaling factor and it is therefore refined separately with respect to the entire set of structural amplitudes, with the remaining variable parameters fixed. Recently an alternative procedure has also been used—the determination of the scaling factor from hard γ-ray diffraction data[14] or from neutron diffraction data.[15]

As already stated, the distribution of $\delta\rho$ is less subject to the influence of the termination of the series than the distribution of ρ, but in the case of $\delta\rho$ it is more difficult to apply the corresponding correction. There is a prospect that in the solution of this problem (both for ρ and $\delta\rho$) it will be possible to abandon the traditional Fourier method, having replaced it by the entropy maximisation method. The latter makes it possible also to reduce the role of random errors, which increases the resolution of the electron density maps.[16,17] The essential feature of the method of Kuz'min et al.[18] consists in the fact that the coefficients of the series, corresponding to weak reflections and assumed to be zero in the usual XRDA scheme, are found from the conditions

$$S = -\int \frac{\rho(\mathbf{r})}{F(000)} \ln \frac{\rho(\mathbf{r})}{F(000)} d\mathbf{V} \to \max.$$

Here the function $\rho(\mathbf{r})$ is regarded as the distribution of the probability density, the best distributions being selected from all the distributions agreeing with the available information. The application of this procedure requires, however, a large amount of computer time.[16]

Hitherto we have spoken of the improvement of the determination of the moduli of structural amplitudes. Another possibility of refining the distributions of ρ obtained from a diffraction experiment consists in improving the calculation of the initial phases. In the standard XRDA, they are calculated in the anisotropic harmonic approximation of spherically scattering atoms. In order to obtain accurate distributions of ρ, use is made of better models: the *L*-shell method (the cleaved atom method), the κ-method, the two-centre models of charge clouds on bonds and lone pairs (Stewart, Hellner), and different versions of the multipolar models (Coppens, Hirshfeld, Stewart, Tsirel'son). All these methods, which are mentioned in order of increasing complexity, have been described in a review.[7] The importance of allowing for the anharmonicity of thermal vibrations has been confirmed[19] in relation to γ-aminobutanoic acid. The methods listed have been compared in two communications.[20,21]

The most complex (and because of this the most flexible) of the models enumerated contain a large number of parameters, which sometimes reaches the number of the accessible independent structural amplitudes. The problem of eliminating the correlations between these parameters has therefore arisen. Here the use of neutron diffraction and spectroscopic data as well as the superposition of additional physical conditions, in particular the determination of the relation between the distribution of ρ and the one-determinant wave function of the crystal, are helpful. One of the new examples of this approach has been provided by Frichberg.[22]

A relatively new step has been the use of experimentally measured initial phases. The anomalous scattering effect can be used for this purpose. In recent years, such studies have been carried out. In the presence of heavy atoms, anomalous scattering can be optimised by adjusting the wavelength of the synchrotron radiation.[23] It has also been suggested[24] that the initial phases be determined from intensity measurements at two wavelengths close to the characteristic wavelength, the wavelength of the X-ray generated by the electron beam directly in the crystal investigated being determined by the angle of incidence of the electrons relative to the modal plane. This method is applicable also to substances without heavy atoms, for example, to oxygen-containing organic compounds.

The method based on analysis of three-wave diffraction profiles under the conditions of the Renninger effect (interference occurring when two series of planes assume simultaneously the reflecting position) has been applied in practice.[12,25,26] This method makes it possible to determine experimentally the initial phases of certain reflections. A precision study of the Si crystal (involving measurement of the intensities and determination of the initial phases of the "forbidden" reflections) made it possible to increase by an order of magnitude the accuracy of the determination of $\delta\rho$ [mean square error $\sigma(\delta\rho) \simeq 0.005$ e Å^{-3}] [25] and to discover on the pseudostatistical $\delta\rho$ distribution map a fine effect involving the splitting of the peak on the Si—Si bond into two components.[26]

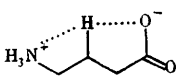
The experimental determination of the initial phases on the basis of three-wave diffraction apparently represents the most promising aspect of studies of this kind. However, despite the clear advantages of the direct experimental methods for the determination of the initial phases listed above, they still remain too complex to hope for their rapid and extensive application on a large scale.

III. Primary interpretation of electron density distributions

The distribution of the total electron density contains in principle exhaustive information about the nature of intramolecular and intermolecular interactions[10] (and also about all the one-electron properties of the system[7]), but its direct interpretation is difficult.[8] To facilitate the use of such information, additional procedures and concepts are introduced. They will be examined in the present Section (in relation to examples taken from studies in recent years).

The simplest numerical characteristics of continuous distributions of ρ are the effective point moments, in particular the atomic and bond charges. They can be obtained not only at the refinement

stage (in the model of multipolar pseudoatoms or charge clouds) but also subsequently from the $\delta\rho$ distribution constructed. For example, it has been proposed[27] that $\delta\rho$ peaks be fitted by ellipsoids of rotation and that the bond charge be calculated by integration with respect to the entire volume of the ellipsoid. Different procedures for the separation of $\delta\rho$ into contributions corresponding to individual atoms have been compared in another communication.[28] Atomic charges are useful in the calculation of the properties of the crystal (for example, in the calculation of the electrostatic field gradients at nuclei[7] or of the Coulombic components of the intermolecular interaction[6]) and in the analysis of the "electronic structure" of molecules. Thus the employment of pseudoatomic charges, determined from diffraction data, made it possible to detect the inductive effect in molecules of barbital[29] and tetrafluoroterephthalodinitrile[30] and an unusual methylene hydrogen bond in γ-aminobutanoic acid:[9]



In order to weaken the dependence of the effective atomic charge on the method used to subdivide the continuous distribution, it has recently been suggested[31] that the charge of a "local region", defined as the sum of the effective charges on a given atom and on the neighbouring atoms linked directly to it, be brought into correspondence with each atom. This approach yields more "reasonable" values. For example, the carbon atoms of an aromatic nucleus in the naloxone ion $C_{19}H_{22}NO_4^+$ have been found to carry a larger negative charge than the aliphatic carbon atoms, the nearest N and O atoms carrying the greatest negative charge.

Pseudoatomic moments can also be used to bring the parametric description of ρ closer to orbital ideas.[32] The calculation of the electron populations of the *d*-orbitals of Fe^{2+} in the porphyrin complex with the aid of a multipolar model yielded values close to those expected for the high-spin $^5F_{2g}$ configuration. The observed deviations indicate the presence of dative bonds with the ligands.[33] A more general approach consists in the application of the valence form-factors, i.e. the atomic scattering factors, taking into account the valence state and not averaged with respect to orientations: this approach also yields *p*-orbital populations.[34]

Another way of interpreting the distribution of ρ in chemical terms involves the density matrix method.[7] In this method the calculation of the elements of the bond charge-order matrix elements involves adjustment to X-ray diffraction data. An unambiguous calculation is achieved by imposing an additional condition involving the minimisation of the energy functional.[35] However, the finite nature of the basis set makes it possible to obtain satisfactory results even without this requirement.[36] An alternative way of finding the wave function from the distribution of ρ^{stat} is described at the end of this Section.

The rigidity of the multipolar pseudoatoms[7] (i.e. the independence of the populations of the thermal parameters) gives rise to the possibility of separating the effects of chemical bonds from the thermal "spreading" of ρ and of constructing the pseudostatic electron density ρ^{stat}. When such construction is entirely adequate, the results should be independent of the experimental temperature. So far it has not been possible to achieve this.[37] A more detailed analysis of the influence of thermal motion on the distribution of ρ has been described.[38–40]

According to certain investigators, the clearest form in which the results of a precision X-ray diffraction analysis can be represented is in terms of the electrostatic potential φ and the deformation electrostatic potential $\delta\varphi$.[41] The application of this method to organic crystals is extremely fruitful in the analysis of the effects of the chemical bond, intermolecular interaction, and reactivity. These questions have been discussed in other reviews,[42,43] where the principal formulae can be found.

We may note the latest studies in this field. A method for the subdivision of the crystal space into molecules with the aid of the electroneutrality principle has been proposed[44] and applied to dicyanodiamide. The $\delta\varphi$ distribution maps for the $C_{13}H_8N_2$ molecule have made it possible[45] to discover the weakest bond in the cyclopropane ring: whereas on other bonds the deformation potential $\rho\varphi$ has a negative minimum, on this bond it is close to zero. This agrees with the chemical properties; even at room temperature, the substance undergoes unimolecular isomerisation with dissociation of the given bond.

The study of phosphorylethanolamine $C_2H_8NO_4P$ [46] showed that the large (in absolute magnitude) negative potential in the region of the ester oxygen atom of the phosphate group is not saturated even on formation of a hydrogen bond by the other oxygen atom of the same group. The layer made up of such molecules serves as a model of a phospholipid membrane and near the surface has regions of positive and negative potential, which enables the molecules of the layer to form hydrogen bonds with both donors and acceptors. Such "amphoteric" behaviour was not predicted in quantum-chemical calculations for an isolated molecule.

The study of the molecular complex of thiourea with parabanic acid $CH_4N_2S.C_3H_2N_2O_3$ [47] revealed saddle points in the φ distribution of approximately equal height in the regions of the N–H...O and N–H...S hydrogen bonds formed by the molecules of this layer. It was concluded on this basis that the energies of the two bonds are similar despite the considerable difference between their lengths (0.27 Å). It has also been shown that the interaction of molecules of different layers does not take place as a result of charge transfer but involves short contacts between the S atoms and the C–C bonds: there is a broad saddle point in the distribution of φ in this region.

The electrostatic potential of the molecule permits a correct inference about its intermolecular interactions only in those cases where interactions involving monopoles predominate in electrostatic forces (for example, on protonation). The "dipolar electrostatic potential",[48] which describes the optimum orientation and energy of a single dipole located at a certain point in the electron distribution (in particular on the van der Waals surface of the molecule) is more suitable for characterising the interaction with a polar uncharged molecule. Such maps show, for example, that the preferred direction along which a nucleophile approaches a formaldehyde molecule does not lie in the plane of this molecule.[48]

The force density method,[49] consisting in the analysis of the distribution of the modulus of the electrostatic force density $f_A(\mathbf{r}) = \rho(\mathbf{r})/(\mathbf{r} - \mathbf{R}_A)^2$, acting on the nucleus A, located at the point $\mathbf{R}_A$, from the side of the electron density at the point $\mathbf{r}$ and diminishing (or intensifying) the destabilising repulsion from other nuclei, is close to the electrostatic potential method. For example, the function $f_N(\mathbf{r})$ for the N_2 molecule has peaks at the centre of the bond (stabilisation) and on the line obtained by producing the bond to the rear at the given atom (destabilisation). In the LiF molecule, similar $f_F(\mathbf{r})$ peaks have been displaced towards the F nucleus, while $f_{Li}(\mathbf{r})$ has a single peak coinciding with the centre of the F atom. Apart

from the differences between covalent and ionic bonds, the force density method makes it possible to investigate the character of the chemical bond in complex polycyclic structures.

However, analysis of the φ and f distributions as well as the use of local (effective) electrostatic characteristics apparently solves only a limited range of specific problems. The most universal and most widely used means for the primary interpretation of the distribution of ρ is provided by the deformation electron density $\delta\rho$ function, which is extremely sensitive to details of the electronic structure of molecules and crystals. The regions of positive values of $\delta\rho$ are those where electron density accumulates compared with the precrystal, consisting of non-bonded atoms. However, the absence of positive $\delta\rho$ maxima on the bond (and even the negative values of $\delta\rho$), which sometimes occur in the case of bonds formed by electronegative atoms (N, O, F, etc.), by no means imply the absence of a bond.

One of the causes of such anomalies consists in the fact that thermal motion "blurs" the $\delta\rho$ map. Thus the dynamic function $\delta\rho$ for crystals of *p*-nitropyridine *N*-oxide $C_5H_4N_2O_2$ [50] has low values in the region of the $\rangle N\rightarrow O$ bonds and the lone pairs of the O atom, whereas considerable peaks appear in these regions on maps which are constructed with the aid of the multipolar resolution and afford a pseudostatic picture. Furthermore, the large angle procedure for the refinement of thermal parameters can lead to the smoothing of the anisotropy of the electron distribution. This effect causes a particularly marked reduction of the height of the LEP peaks, which are located closer to the nucleus than the peaks on the bonds.[51]

However, the type of bond has a decisive influence on the height of the $\delta\rho$ peak. The causes of the redistribution of electron density, arising from the preparation of the atoms of the premolecule for bonding (promotion of electrons, orientation, polarisation, and hybridisation of orbitals) and from the formation of bonds proper (interference of the orbitals and charge transfer) have been listed[52] in terms of hybrid orbitals (HO).

We shall consider initially the effects due to the formation of bonds. For a bond between atoms 1 and 2, the bonding molecular orbital, made up of the singly populated HO ψ_1 and ψ_2, assumes the following form in terms of the LCAO MO approximation:

$$\Psi = (1+2\lambda S+\lambda^2)^{-1/2}(\psi_1+\lambda\psi_2),$$

where S is the overlap integral. The electron density of this orbital is

$$\rho_{MO} = 2\Psi^2 = (1+2\lambda S+\lambda^2)^{-1}(2\psi_1^2+2\lambda^2\psi_2^2+4\lambda\psi_1\psi_2) =$$
$$= (\psi_1^2+\psi_2^2)+(1+2\lambda S+\lambda^2)^{-1}(4\lambda\psi_1\psi_2-2\lambda S(\psi_1^2+\psi_2^2))+$$
$$+(1+2\lambda S+\lambda^2)^{-1}(1-\lambda^2)(\psi_1^2-\psi_2^2) = \rho_0+\Delta\rho_i+\Delta\rho_{ct}.$$

For HO with similar energies, $\lambda \simeq 1$ and $\Delta\rho_{ct} \simeq 0$. The deformation density is then $\Delta\rho_i$ and is approximately proportional to the overlap density $\psi_1\psi_2$ at the maximum. By analogy with the interaction of light waves, this effect is referred to as interference. With increase in bond length, the overlap density and hence $\Delta\rho_i$ diminish. Furthermore, for large bond lengths (especially between transition metal atoms), electron correlation, not taken into account in the MO method, makes an appreciable contribution to the decrease of $\Delta\rho_i$.[51]

If the interacting HO are identical, then the quantity $\Delta\rho_i$ is a maximum at the centre of the bond. On the other hand, if they have similar energies but different extents in space, the greatest overlap density (and hence the $\Delta\rho_i$ maximum) should be attained closer to the centre of the more compact orbital. Even greater changes in elecron density are induced by differences between the orbital energies. The energy of the HO diminishes with increase in its electronegativity and s character. If the energy of ψ_2 is greater than that of ψ_1, then $\lambda < 1$ and the charge transfer effect $\Delta\rho_{ct} \simeq \psi_1^2 - \psi_2^2$ arises. Ultimately the $\Delta\rho$ peak shifts in the direction of the atom 1.

We shall now consider a hypothetical distribution of electron density of the premolecule on transition of the atoms to the valence state (i.e. during the preparation of the atoms for the formation of a bond). According to the concept of hybridisation, when a HO is formed with participation of the atomic s and p orbitals, the populations n_s and n_p change (electrons are promoted from the s sublevel to the p sublevel). In particular, in the case of ideal sp^3-hybridisation of the C atom, $n_s = 2$, $n_p = 2/3$, and $n_s' = n_p' = 1$; for the O atom, $n_s = 2$, $n_p = 3/4$, and $n_s' = n_p' = 6/4$. This leads to some transfer of the electron density of a spherical atom from its centre to its periphery. The subsequent orientation of the HO is determined by the nearest neighbours of the atom in the premolecule and fixes both the position of the singly populated HO involved in the bonds and the doubly populated HO (i.e. lone pairs). After the orientation of the HO, the change in the population of the p orbital directed along the bond line is

$$\Delta n_p = {}^3/_4 + {}^1/_{12}(n_2+n_3+n_4) - n_p,$$

where the numerical coefficients correspond to the contributions of the p orbital to the sp^3-HO with the populations n_i. For the carbon and oxygen atoms, $\Delta n_p = 0.33$ and -0.17, i.e. ρ accumulates between carbon atoms and diminishes between oxygen atoms, while between oxygen and carbon atoms the electron density shifts from oxygen to carbon. Electrons always accumulate in the direction of the LEP.

$$\Delta n_p' = {}^3/_2 + {}^1/_{12}(n_2+n_3+n_4) - n_p.$$

However, the simple scheme described does not take into account certain fairly important effects. For example, under the influence of the environment the atomic orbitals undergo a change in shape (are polarised). In particular, the 1s orbital of the H atom contracts slightly on formation of the bond. Furthermore, the differences between the electronegativities of the substituents or steric stresses can lead to deviation of the hybrid orbitals from the ideal sp^3, sp^2, and sp orbitals. Finally, the populations of the interacting orbitals can differ from unity. Thus, in the $Mn_2(CO)_{10}$ dimer examined below, the population of the d orbitals forming the Mn–Mn bond diminishes under the influence of the ligand field, which is in fact the main reason for the absence of the $\delta\rho$ peak on this bond.[51] However, despite the above stipulations and effects due to the formation of bonds, the height of the $\delta\rho_{max}$ peak usually varies in parallel with the quantity $n_p' - n_p$ according to Angermund et al.;[10] this indicates the predominance of the orientation effect.

In order to isolate the chemical bond effect in a pure form, the sum of the electron densities of the oriented atoms $\rho_0^{(or)}$ was subtracted[52,53] from the total function ρ; the resulting function was called the chemical deformation density $c\delta\rho = \rho - \rho_0^{(or)}$.

When the functions $c\delta\rho$ are used, we in fact abandon a universal reference standard. The next step in this direction is taken when the "fragment-formation" density $f\delta\rho$ is introduced;[54] this is obtained when the electron density of the fragments is subtracted from the total function ρ. The $f\delta\rho$ maps can be used to investigate the redistribution of electrons when the reacting species interact.

In particular, in the study of coordination compounds, it is natural to differentiate the central atom and the ligands as the fragments. This was done in a quantum-chemical study of the distribution of ρ in the $Co_2(CO)_8$ molecule,[54] which showed that the interaction of a CO molecule with a metal atom leads to the outflow of electron density from the C–O axis into the region of the *p* orbitals of oxygen and carbon perpendicular to this line. The function $f\delta\rho$ makes it possible to observe the redistribution of electrons on formation of a covalent bond between radicals or molecules. The peak due to the Mn–Mn bond, which is absent from δρ maps, and also the displacement of the lone electron pairs of the oxygen atoms in the equatorial CO groups in the direction of the "foreign" Mn atom can be seen on the $f\delta\rho[Mn_2(CO)_{10}-2Mn(CO)_5]$ map constructed[54] from the results of non-empirical calculations, while on δρ maps the differences between the electron distributions of the axial and equatorial ligands are inappreciable.

It has been shown[55] with the aid of $f\,\delta\rho$ that, on formation of the $H_3N{\rightarrow}BH_3$ donor–acceptor bond, an appreciable decrease in electron density is observed in the first place in the region of the p_σ orbital of the B atom, extended along this bond, with the simultaneous decrease in electron density on the corresponding orbital of the N atom and on the ammonia H atoms (the σ-donor effect of nitrogen) and in the second place there is a small transfer of electron density from the perpendicular p_π orbital of the B atom to the orbital of the N atom oriented in parallel (the π-acceptor effect).

The above examples of quantum-chemical calculations indicate the possibility of the effective employment of the $f\delta\rho$ function also for the primary interpretation of the experimental distributions of ρ.

With the aid of difference functions, it is possible to discover also the redistribution of electrons under the influence of external forces. Thus the change in electron density in the H_2O molecule under the influence of an external homogeneous electrostatic field is demonstrated by "polarisation" deformation density $p\,\delta\rho$ maps.[56] In order to discover the effects of the ionic environment in the H_2O molecule and in the $HC_2O_4^-$ ion, the distributions of the "double" deformation density $d\delta\rho = \delta\rho' - \delta\rho$ were constructed, the $\delta\rho'$ distributions being obtained by means of a non-empirical calculation modelling the influence of the crystal structure by point charges.[57]

In the study of intermolecular interactions (including hydrogen bonds and other specific contacts), the "molecular-deformation" density $m\,\delta\rho$ (the difference between the experimental function ρ in the molecular crystal and the superposition of the molecular distributions of ρ calculated for the experimental geometry of the molecules) may prove useful. The $m\,\delta\rho$ maps, constructed for formamide[58] and oxalic acid,[59] reflect the influence of intermolecular interactions, not only on the atoms involved in hydrogen bonds, but also on the inner parts of the molecule.

A fundamentally different and extremely promising procedure for the primary interpretation of the function ρ (topological analysis) was developed by Bader and co-workers (see Refs. 60–62 and the bibliography quoted therein); this method provides one of the possible justifications of the qualitative concept of the classical theory of molecular structure. The principles of Bader's theory are described below and the results of the latest studies of his group as well as the applications of this approach to the experimental distributions of ρ are examined.

The topological properties of the function $\rho(\mathbf{r})$ are revealed in the analysis of the vector field of the gradient $\nabla\rho(\mathbf{r})$. Here one uses a series of auxiliary concepts (they are illustrated by Fig. 1, where the vector field of the $CH_2{=}CHF$ molecule is presented as an example).

1. The surface *S*, at each point of which the vector flux of the gradient is zero [i.e. $\nabla\rho(\mathbf{r}).n(\mathbf{r}) = 0$, where *n* is the normal] is called the zero flux surface.

2. The curve such that the tangent to each point on it coincides with the direction of the gradient vector is referred to as the trajectory or gradient line. Each trajectory is one of the solutions of the equation $d\mathbf{r}(s)/ds = \nabla\rho[\mathbf{r}(s)]$ and is specified by the formula

$$\mathbf{r}(s) = \mathbf{r}_0 + \int_0^s \nabla\rho(\mathbf{r}(t))\,dt.$$

3. The point at which the gradient $\nabla\rho(\mathbf{r})$ becomes zero is called critical (the point $\mathbf{r}_c$). This point is characterised by the rank λ and the symbol σ. The rank λ is equal to the number of non-zero values of the curvature matrix (Hessian) with the elements

$$H_{ij} = (\partial^2\rho/\partial\mathbf{r}_i\partial\mathbf{r}_j)\,\mathbf{r}=\mathbf{r}$$

and the symbol σ represents the difference between the number of positive and negative eigenvalues.

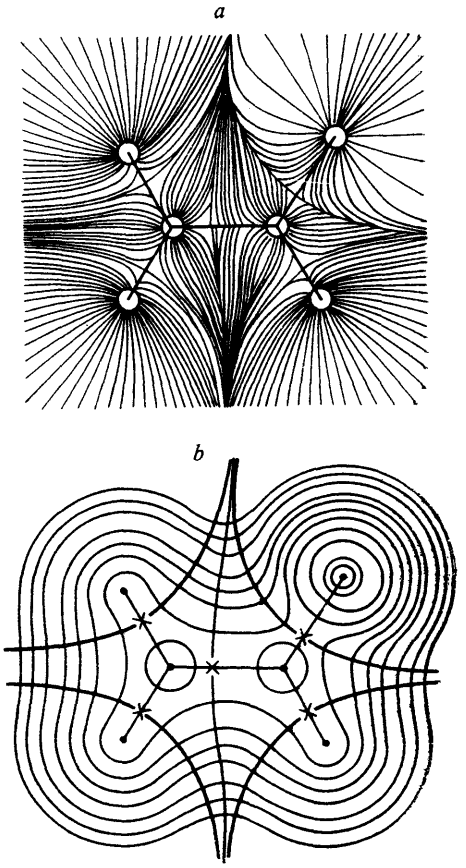


Figure 1. Topological analysis of the vector field of the $CH_2{=}CHF$ molecule (section coinciding with the plane of the molecule): (*a*) gradient lines terminating at the atomic nuclei, bond lines, and zero flux surfaces dividing the basins of the atoms are shown; (*b*) the critical points (3, –3) and (3, –1), the bond lines, and the zero flux surfaces against the background of the distribution of electron density are shown.

The critical points (λ, σ), for which $\lambda < 3$, are degenerate (unstable): for any change in the function $\rho(\mathbf{r})$, induced by the shift of the nuclei, these points either vanish or break up into a certain number of non-degenerate (stable) critical points. Such points are encountered rarely but play an important role because they indicate the possibility of structural changes in the system.

Non-degenerate critical points (for which $\lambda = 3$) can refer to one of four types: (3, −3) (maxima), (3, −1) and (3, +1) (saddle points), (3, +3) (minima).

The critical point of the type (3, −3) represents a set of ends ($s \to \infty$) of gradient trajectories which do not lie on the surfaces S; thus the role of "sinks" (attractors) of the vector field $\nabla\rho$ is attributed to these points.

The set of trajectories terminating at the given attractor forms the "basin" of this attractor. Two neighbouring basins are separated by the surface S, on which is located the critical point of the (3, −1) type [crossing point (pass)]. The trajectories located on the surfaces S terminate at the critical points (3, −1); a pair of trajectories, terminating at two neighbouring attractors and forming the "bond line", arise from each such point. Along this line, the electron density ρ is a maximum, i.e. small displacements perpendicular to this line lead to a decrease in ρ.

In Bader's theory, it is assumed that the minima in the function ρ coincide with the atomic nuclei.† Nuclei are then connected by bond lines; the assembly of nuclei and bond lines forms a molecular graph. The atom is defined as a combination of the attractor (nucleus) and its basin.

Bader's theory also includes the analysis of the "structural stability" of molecular systems, whose description is outside the scope of the present review.

Various methods for detecting the location of atoms in a molecule have been described in the literature.[64,65] However, the condition of the fulfillment of the principle of minimum action not only for the entire system (molecule) but also for its subsystems (atoms) requires that atoms be bounded by zero flux surfaces, as is done in Bader's theory. In this case, the atom in a molecule is described by the same equations of motion and theorems (for example, the virial theorem or the Ehrenfest theorem) as those applicable to the total system. Any property of an atom (charge, dipole moment, kinetic and potential energies) is calculated as the average value of a one-particle operator, which, however, is averaged only with respect to the volume of the atomic basin and not the entire space.

The topographical characteristics proposed by Bader also make it possible to describe important properties of interatomic bonds. The ratio of the bond length l to the length of the internuclear vector and the distance from the corresponding critical point (3, −1) to this vector serve as a measure of the curvature of the bond in molecules with steric strain or in non-equilibrium molecular systems. The degree of angular strain is measured as the difference between the angle between the bond lines and the angle between the bond axes.

The energy of the AB bond is defined as

$$E_{AB} = \alpha N_{AB} / (\mathbf{R}_A - \mathbf{R}_B)^2,$$

where α is a dimensionless coefficient (it is assumed that it is equal to 3 for the bonds in alkanes) and N_{AB} is a measure of the number of bond electrons. The latter quantity is assumed to be zero for free atoms, while for the deformed atoms in the molecule

$$N_{AB} = (\mathbf{R}_A - \mathbf{R}_B) \oint \rho(\mathbf{r})\, \mathbf{n}_A(\mathbf{r})\, dS_{AB},$$

where S_{AB} is the area of the zero flux surface separating two basins and $\mathbf{n}_A(\mathbf{r})$ is the unit vector of the normal to S_{AB} directed from the atom A to the outside.

Important conclusions about the character of the bond can be reached from the analysis of the distribution of ρ in the region of the critical point (3, −1). By definition, the Hessian at the critical point has two negative ($|\lambda_1| \geqslant |\lambda_2|$) and one positive ($\lambda_3$) eigenvalue, each of which defines the curvature of ρ along the corresponding eigenvector, i.e. at right angles to the bond (λ_1 and λ_2) and along the bond (λ_3). The multiplicity n of the C−C bond can be calculated from the electron density $\rho(\mathbf{r}_c)$ at this point. This is done by interpolating between the values of $\rho(\mathbf{r}_c)$ in the C_2H_6, C_6H_6, C_2H_4, and C_2H_2 molecules, for which $n = 1$, 1.5, 2, and 3. The corresponding relation is expressed by the formula $n = \exp[6.458(\rho_c - 0.252)]$.

The bond ellipticity ε [where $\varepsilon = (\lambda_1/\lambda_2) - 1$] is a measure of the deviation of the charge distribution along the bond trajectory from radial symmetry. This quantity is sensitive to the amount of "π character" of the bond. If a single bond is conjugated with a double bond, then calculation for the former yields $n > 1$ and $\varepsilon > 0$.

However, the presence of the critical point (3, −1) is only a necessary but not a sufficient condition for the existence of the covalent bonds between two atoms: such points exist in ion pairs, in molecular complexes with hydrogen bonds and charge transfer, and also in premolecules. The predominance in the internuclear region of the potential energy of the electrons (negative in sign) over the positive kinetic energy has been postulated as a sufficient condition. This empirical postulate has different mathematical expressions. Bader uses for this purpose the "charge concentration function": $g = -\nabla^2\rho$, where $\nabla^2\rho$ is the Laplacian of the electron density ($\nabla^2\rho = \partial^2\rho/\partial x^2 + \partial^2\rho/\partial y^2 + \partial\rho/\partial z^2$), expressing the overall curvature at the point with the coordinates x, y, and z and equal, according to the virial theorem, to twice the sum of the kinetic and total energies of the electrons at this point. Other workers[66] consider the total energy of the electrons (the sum of the kinetic and potential energies) at the critical point of the bond.

If $g(\mathbf{r}_c) > 0$, then the quantity ρ at the critical point exceeds its average value in a small region near this point, i.e. the charge accumulates in the internuclear space and the bond is regarded as covalent. The only exception is the F_2 molecule, which can be explained by the anomalously high intraatomic correlation of the electrons. For an ionic bond, $g(\mathbf{r}_c) < 0$. Here the function ρ exhibits a plateau in the plane perpendicular to the bond line and the positive values of g are localised near the nuclei on either side of the plane. The same picture is observed for hydrogen bonds and van der Waals interactions.

More detailed topographical analysis of the function g also yields useful results. In an isolated atom, the maximum values of g are observed at the point corresponding to the nucleus and on $n - 1$ concentric spheres, where n is the principal quantum number. Since an evident analogy with the shell model of the atom is to be seen

† In a recent non-empirical study of free Na_m clusters ($m = 2$, 4),[63] ρ maxima were observed between nuclei, the Na atoms forming bonds only via these "pseudoatoms". Apparently this feature is characteristic of a metallic bond and the experimental observation of ρ maxima at the centres of the vacancies in spherical packings is to be expected, for example, for crystals of alkali metals and beryllium.

here, the outer sphere with an increased charge concentration is referred to as the valence shell. When the atom forms chemical bonds, the valence shell is distorted and loses the constancy of g at each of its points; local g maxima appear on it, i.e. two dimensional attractors (2, –2) and between them saddle points (2, 0) appear on it. The trajectories ∇g, originating from the saddle points, divide the valence shell into two-dimensional basins each of which contains one maximum. If $g > 0$ at a given maximum, then a region of increased charge concentration, i.e. a region where $g > 0$, corresponds to it (evidently such regions can overlap).

In Bader's view, analysis of maps of the distribution of the function g provides a physical justification of the concept of electron pairs. Furthermore, the number, positions, and dimensions of the regions with an increased charge concentration agree with Gillespie's ideas[67] of the repulsion of localised pairs, explain Pearson's theory of hard and soft acid and bases,[68] and can serve as a basis for the determination of the direction of electrophilic and nucleophilic attack on the orientation of the reacting molecules at the start of the reaction. Bader believes that this approach is more correct than the electrostatic models usually employed nowadays, because molecules approaching one another "see not the charges on the atoms and not the distribution of the electrostatic potential but the system of local discharge and charge concentration centres described by the electron density Laplacian". The predictions of the intramolecular and intermolecular interactions, presupposing the mutual attraction of regions with different signs of g, have therefore proved to be extremely successful.

Thus the minimum in g on the valence shell surface of the carbonyl carbon atom is located in the direction forming an angle of 110° with the C=O bond. Accordingly, in crystal structures with shortened contacts between oxygen and carbonyl carbon atoms the O...C=O angle is usually close to this value.

When the molecule contains competing active centres, analysis of the function g makes it possible to predict the preferred direction of the reaction. For this purpose, one uses the concept of the "hardness" of the active centre.[68] The interaction of "like with like", i.e. of a harder nucleophile with a harder electrophile and conversely, is found to be preferred. According to Bader, the hardness of the nucleophile (electrophile) increases with decrease in the distance between the maximum (minimum) and the nucleus and also with increase in the absolute magnitude and curvature of g at the extremum.

The approach developed by Bader and co-workers has been used recently to interpret the results of non-empirical quantum-chemical calculations for an increasing range of molecular systems (hydrocarbons, carbonium ions, carbenes, complex compounds, "non-rigid" molecules, molecular dimers). With the aid of this approach, it is possible to investigate intermolecular and intramolecular hydrogen bonds and the effects of hyperconjugation and heteroaromaticity. It has been shown[69] that the properties of atoms and bonds and the influence of substituents on the position of the critical point can be associated with simple orbital models. The fact that the electron distribution in the premolecule ρ_0 contains valuable chemical information is somewhat unexpected: in particular, it makes it possible to divide the molecule into pseudoatomic fragments.[70]

It was noted previously that the Bader approach is promising not only as regards the calculated theoretical distributions $\rho(\mathbf{r})$ but also as regards their experimental values. The first studies on these lines[71,72] confirmed this conclusion. The ethane molecule in a crystal was investigated on the basis of the topographical analysis of the experimental function ρ taking into account the specific limitations of the experiment.[71] In contrast to the free molecule, here one observes a non-zero ellipticity of the C–C bond, which can be treated as partial double bond character due to the influence of the environment. However, this effect can be explained also by the imperfection of the method: the static distribution of ρ in the molecule is regarded as the sum of the static function ρ_0 of the premolecule and the dynamic function $\delta\rho$, which precludes the complete exclusion of the influence of thermal motion. A $\nabla^2\rho$ map has been used[72] to describe non-classical many-centre bonds in the pseudocubic V_4S_4 cluster. The conclusion that the V–V and V–S bonds are covalent, reached on its basis, served as a significant complement to the $\delta\rho$ map.

Thus topographical analysis of the distribution of ρ is a powerful instrument and reveals many hidden features of electron density. However, like any universal method, it does not enable one to discover fully the chemical individuality of the compound. Comparision of the distributions of ρ for the given substance and its chemical analogues helps to view this individuality from different aspects.

The necessity for a quantititative comparison of two charge distributions arises also in other cases (comparison of theory and experiment, comparison of the results of two different calculations or two experimental studies, etc.). Such comparison can be carried out on three levels: (1) the integral level (the outcome is expressed by a single parameter); (2) the local level (the outcome is represented by a set of values); (3) the continuous level (the outcome of the comparison is a continuous function).

The Carbo index serves as an integral characteristic of molecular similarity.[73] For isoelectronic molecules, it can be reduced to the generalised Polanski number:

$$K_{12} = \frac{\int \rho_1\rho_2 dV}{\left(\int \rho_1^2 dV\right)^{1/2}\left(\int \rho_2^2 dV\right)^{1/2}} \simeq \frac{N}{2} tr\,(P_1P_2),$$

where N is the number of electrons and P_1 and P_2 are the density matrices of the molecules 1 and 2 formulated in terms of a single basis set. The quantity K_{12} depends on the method used to superimpose the molecules. On the basis of the similarity index for the reactants and products, it is possible, for example, to predict the stereospecificity of pericyclic reactions.[74]

Without dwelling in detail on the local comparison of the distributions of ρ, we shall mention only that the discrete characteristics, listed at the beginning of this section, or the properties of atoms and bonds considered by Bader can serve as parameters of such comparison.

Continuous comparison yields most information but is usually carried out at a qualitaltive level involving the visual comparison of two $\delta\rho$ maps. For example, the differences between two crystallographically independent thiourea molecules (the reasons for the differences were not discovered)[21] and three forsterite crystals (the reason is the inadequate allowance for the extinction manifested in different ways)[12] were observed in precisely this way.

A more complete and objective result is provided by a quantitative continuous comparison involving the construction of difference density maps. However, even for small differences between geometrical parameters of the molecular systems 1 and 2 compared, such constructions become ambiguous. Even in the simplest case, involving the comparison of two N_2 molecules with internuclear distances of 1.09 and 1.11 Å, one can superimpose either the centres of gravity or one pair of nuclei. In the former case, the

difference density map[75] shows the accumulation of ρ between the nuclei as the latter approach one another, while in the second it shows the accumulation of ρ in the postnuclear region and in both cases there is a pair of intense peaks (positive and negative) corresponding to the nuclear displacements. The "point" generalised-difference density $\Delta\rho'$ makes it possible to avoid the latter false effect and at the same time to discover the first two. Such density was derived by Steiner:[75]

$$\Delta\rho'(\mathbf{R}) = \rho_1(\mathbf{f}_1(\mathbf{r})) - \rho_2(\mathbf{f}_2(\mathbf{r}')).$$

where $\mathbf{r}$ and $\mathbf{r}'$ are the coordinates of the points corresponding to one another in the molecules 1 and 2 and $\mathbf{R} = \mathbf{f}(\mathbf{r})$ is the function of the change of variables mapping the coordinates of the nuclei of the first molecule $\mathbf{r}_i$ on the ideally disposed reference points $\mathbf{R}_i$. The integral of ρ with respect to the volume of the molecule, which is equal to the number of electrons, must be invariant relative to such change of variables:

$$\int \rho(\mathbf{r})\, d\mathbf{r}^3 = \int \rho''(\mathbf{R})\, d\mathbf{R}^3 = \int \rho''(f(\mathbf{r}))\left|\frac{d^3\mathbf{R}}{d^3\mathbf{r}}\right| d\mathbf{r}^3.$$

In order to take into account this factor, a "volume" generalised-difference density $\Delta\rho''$ was constructed:

$$\Delta\rho''(\mathbf{R}) = \rho_1(\mathbf{r})\left|\frac{d^3\mathbf{f}_1(\mathbf{r})}{d^3\mathbf{r}}\right| - \rho_2(s)\left|\frac{d^3\mathbf{f}_2(\mathbf{r}')}{d^3\mathbf{r}'}\right|,$$

where $|d^3\mathbf{f}_1(\mathbf{r})/d^3\mathbf{r}|$ is the Jacobi determinant.

In the case of the N_2 molecule, the distribution of $\Delta\rho''$ on approach of the nuclei proved to be similar to the distribution of δρ and was interpreted as partial transfer of electrons from the p_π to the p_σ orbital. A similar electron redistribution was noted also in the case of ethane on transition from the eclipsed to the hindered configuration. This effect is not manifested in the rigid rotation of methyl groups and has been observed only with the aid of generalised-difference maps.[75] A significant disadvantage of the study described is an extremely artificial and ambiguous construction of the function $\mathbf{f}$ by the method of segmental-linear interpolation along each coordinate of the Cartesian system. This led to breaks on the $\Delta\rho''$ maps and to a dependence of $\Delta\rho''$ on the choice of direction of the axis.

The coordinate transformation method was also used[76] for the solution of the problem of recovering the wave function from precision XRDA data. The change of variables leaves the nuclei in place and distorts the electron density of the premolecule ρ_0 until it coincides fully with the experimental density:

$$\rho(\mathbf{r}) = \left|\frac{d^3\mathbf{f}}{d^3\mathbf{r}}\right| \rho_0(\mathbf{f}(\mathbf{r})).$$

The transformation $\mathbf{f}$ found from this condition is then applied to the wave function of the precrystal in order to obtain the wave function of the crystal. A local-scaling transformation, in which $\mathbf{r}\|\mathbf{f}(\mathbf{r})$ is used as $\mathbf{f}$. By applying the approach described to the problem of the construction of the generalised-difference density, one can ensure the uniqueness of the function of the change of variables by the requirement for the complete coincidence of the electron densities of the premolecules of the systems being compared.

Another procedure for the quantitative comparison of the charge distributions w_1 and w_2, where $w = \rho, \varphi, \delta\rho, c\,\delta\rho, \nabla^2\rho$, etc., which also ensures the uniqueness of the function $\mathbf{f}$, has been proposed.[77] In particular, it was noted that, in constructing $\mathbf{f}$, it is essential to take into account a series of factors dictated by the physical significance of the problem: the movement of the region near the nuclei without deformation, a strong dependence of the changes in electron density on the changes in the electrostatic potential and the smooth (non-oscillatory) character of these changes. Mathematically the uniqueness of the function $\mathbf{f}$ is ensured by minimising a functional for which one can use the measure of the distortion of space[77] or the information entropy. In the comparison of the distributions of ρ in systems 1 and 2, the function $\mathbf{f}$ can be conveniently represented as a homeomorphism mapping the trajectories $\nabla\rho_1$ onto the trajectories $\nabla\rho_2$. (For molecules or molecular fragments having equivalent structures according to Bader,[60] such homeomorphism exists by definition). In the latter case it is reasonable to impose the requirement that the function $\mathbf{f}$ should bring into coincidence not only the nuclei but also other critical points, as well as the zero flux surface and bond lines.

If a comparison is carried out in order to interpret chemical effects, it is essential to take into account the difference between the thermal vibrations in the systems being compared. Within the framework of the Debye–Waller approximation,[7] this can be done in two ways: by constructing the pseudostatic densities ρ^{stat} or by blurring ρ_2 by the thermal vibrations characteristic of system 1 (with the aid of a convolution transformation) within the framework of the multipolar pseudoatom or solid state models. The function $\Delta\rho''$ constructed reflects the influence of the environment and the substituents on the distribution of ρ in the molecules.[77]

Thus the quantitative comparison of the charge distributions makes it possible (after the appropriate choice of the objects to be compared) to characterise comprehensively the chemical individuality of the molecules and to extract fundamentally new information from X-ray diffraction data.

IV. Trends in the distributions of deformation electron density

Hitherto deformation density maps have been constructed for more than 120 organic compounds. The list, which includes 96 organic substances investigated in this way, has been published in a review.[6] Table 1 lists the organic substances investigated most recently (from 1983 to 1987); among them, one may encounter compounds mentioned in the review of Tsirel'son and Zorkii[6] but reinvestigated recently. The most complex structural formulae of the compounds in Table 1 are shown in Fig. 2.

The available experimental data make it possible to note the following qualitative feature of the distributions of δρ:

(1) the presence of a peak on the covalent bond line (the exceptions are discussed below);

(2) dependence of the form of this peak on the π character of the bond;

(3) the shift of the peak away from the bond axis in sterically strained systems;

(4) asymmetry of the peak of a polar bond;

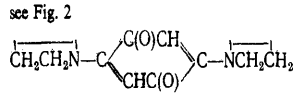
(5) the shift of the peaks of electron-deficient bonds to the bisector of the bond angle (up to the fusion of these peaks);

(6) the presence of a single peak or two peaks in the region of lone electron pairs of the heteroatom;

(7) the slight deformation of the LEP peak on formation of weak and moderately strong hydrogen bonds;

(8) approximate symmetry of the strong hydrogen bond X–H...Y relative to the centre of the XY section.

Table 1. The list of substances investigated.

Empirical formula	Name of substance	Structural formula	Structural class	Refs.
CH_4N_2O *	Urea	$(H_2N)_2CO$	$P\bar{4}2_1m$, $Z = 2(2mm)$	[9]
CH_4N_2S *	Thiourea	$(H_2N)_2CS$	$Pnma$, $Z = 4(m^s)$	[9, 21]
$CH_4N_2S \cdot C_3H_2N_2O_3$	Thiourea–parabanic acid complex	$(H_2N)_2CS \cdot \overline{C(O)NHC(O)NHC(O)}$	$P2_1/m$, $Z = 2(m, m)$	[47]
$C_2H_2O_4 \cdot 2H_2O$ *	α-Oxalic acid dihydrate	$(COOH)_2 \cdot 2H_2O$	$P2_1/c$, $Z = 2(\bar{1}; 1)$	[11, 59, 78]
$C_2H_6NO_2 \cdot Br^-$	Glycinium bromide	$[H_3NCH_2COOH]^+Br^-$		[79]
$C_2H_6N_2O_2$	*N*-Methyl-*N'*-methoxydiazene *N*-oxide	μuc-$CH_3ON{=}N(O)CH_3$	$P2_1/c$, $Z = 4(1)$	[80]
$C_2H_6TeCl_2$	Dimethyltellurium dichloride	$(CH_3)_2TeCl_2$	$P2_1/c$, $Z = 4(1)$	[81]
$C_2O_2Cl_3^- \cdot C_5H_6NO^+$	Hydroxypyridinium trichloroacetate	$CCl_3COO^-[HN(CH)_4COH]^+$	not quoted	[82]
C_2Cl_6P	Bis(trichloromethyl)trichlorophosphorane	$(CCl_3)_2PCl_3$	$R3m$, $Z = 6(3m)$	[83]
$C_3H_2N_2O_2S$	1,6-Dioxa-2,5-diaza-6*a*-thiopentalene	see Fig. 2	not quoted	[84]
$C_3H_4N_2$	2-Aminopropenonitrile	$CH_2{=}C(CN)NH_2$	$P2_12_12_1$, $Z = 8(1)$	[85]
C_3H_9N	Trimethylamine	$(CH_3)_3N$	$P\bar{3}$, $Z = 2$	[86]
$C_4H_2N_2O_4$	2,4,5,6(1*H*, 3*H*)-Pyrimidinetetrone(alloxan)	$\overline{NHC(O)C(O)C(O)NHC(O)}$	$P4_12_12_1$, $Z = 4(1)$	[87]
C_5H_5NO *	2-Pyridone	$\overline{NC(OH)(CH)_3CH}$	$P2_12_12_1$, $Z = 4(1)$	[88]
$C_5H_5N_2Cl$	2-Amino-5-chloropyridine	$H_2N\overline{CHNCHC(Cl)CHCH}$	$P2_1/c$, $Z = 4(1)$	[89]
$C_5H_6NO^+$	See $C_2O_2Cl_3$			
$C_5H_{10}O_5$	β-DL-arabinose	see Fig. 2	$P2_1/c$, $Z = 4(1)$	[15]
$C_6H_2N_4$	1,1,2,2-Ethanetetracarbonitrile	$(CN)_2CHCH(CN)_2$	$P2_1/c$, $Z = 2(1)$	[91]
C_6H_7N *	4-Methylpyridine	$\overline{CHCHNCHCHCHCH_3}$	$I4_1/a$, $Z = 8(2)$	[92]
$C_6H_8F_4$	1,1,4,4-Tetrafluorocyclohexane	$\overline{CF_2CH_2CH_2CF_2CH_2CH_2}$	$Pnnm$, $Z = 2(2/m)$	[30, 93]
$C_6H_{12}N_4O_4$	4,5,10,11-Tetraoxa-1,2,7,8-tetraaza tricyclo-[6.4.1.1^{2,7}]tetradecane	see Fig. 2	$P\bar{1}$, $Z = 1(\bar{1})$	[95]
$C_8D_2O_4F_4^*$	Perdeuteriotetrafluoroterephthalic acid	$C_6F_4(COOD)_2$	$P\bar{1}$, $Z = 1(\bar{1})$	[97]
$C_8N_2F_4$ *	Tetrafluoroterephthalonitrile	n-$C_6F_4(CN)_2$	$Cmca$, $Z = 4(2/m)$	[30, 98]
$C_{10}H_9N_2OSCl$ *	2-(2-Chlorobenzoimino)-1,3-thiazolidine	see Fig. 2	$P2_1/c$, $Z = 4(1)$	[84, 94]
$C_{10}H_{10}N_2O_2$ *	2,5-Bis(ethylenimino)-1,4-benzoquinone		$P\bar{1}$, $Z = 1(\bar{1})$	[99–101]
$C_{10}H_{12}Se_4^{1/x+} \cdot \frac{1}{2}\ AsF_6^-$	Bistetramethyltetraselenofulvalene hexafluoroarsenate	see Fig. 2	not quoted	[96]
$C_{11}H_{12}N_2O_2S$ *	3-Benzimino-4-methyl-1,2,4-oxathiazine	see Fig. 2	$P2_1/c$, $Z = 4(1)$	[84, 94]
$C_{12}H_{11}N_2SiCl_3$	1-(Trichorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline	see Fig. 2	$P2_1/m$, $Z = 2(m)$	[102]
$C_{13}H_8N_2$	Tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene-11,11-dicarbonitrile	see Fig. 2	$P2_12_12_1$, $Z = 4(1)$	[45]
$C_{18}H_{18}$ *	9-t-Butylanthracene		$P2_1/c$, $Z = 4(1)$	[10, 103,
$C_{18}H_{18}$	9-t-Butyl-9,10-Dewar-anthracene		$P2_1/c$, $Z = 4(1)$	104, 105]
$C_{19}H_{22}NO_4^+ \cdot Cl^- \cdot 2H_2O$	Naloxone hydrochloride dihydrate	see Fig. 2	not quoted	[31]
$C_{20}H_{36} \cdot 0{,}86Ar$	Tetra-t-butyltetrahedrane	see Fig. 2	$P6_3/m$, $Z = 6(\bar{1})$	[106]
$C_{20}H_{36}$ *	Tetra-t-butylcyclobutadiene	$C_4(mpem\text{-}Bu)_4$	$C2/c$, $Z = 4(1)$	[107]
$C_{24}H_{20}Si$	Tetraphenylsilicon	$(C_6H_5)_4Si$	$P\bar{4}2_1c$, $Z = 2(\bar{4})$	[108]
$C_{26}H_{22}P_2$	1,1-diphosphinoethylene	$H_2C{=}C(PPh_2)_2$	not quoted	[109]
$C_{26}H_{22}O_2P_2$	1,1-Diphosphinoethylene dioxide	$H_2C{=}C(POPh_2)_2$	not quoted	[109]

*Compounds already mentioned in an earlier review[6] but reinvestigated.

The height of the covalent bond peak

In general, the height of the $\delta\rho_{max}$ peak is not an unambiguous characteristic of the bond strength. Firstly (as a consequence of the lack of standard methods), the differences between the experimental conditions and the refinement procedures lead to a dependence of the results on the method in which it was obtained.[6] Secondly, the thermal vibrations of the molecules and atoms in different structures can "blur" the $\delta\rho$ peaks to different extents, while the static distributions of $\delta\rho$ depend on temperature and the model used as a consequence of the insufficiently accurate allowance for thermal

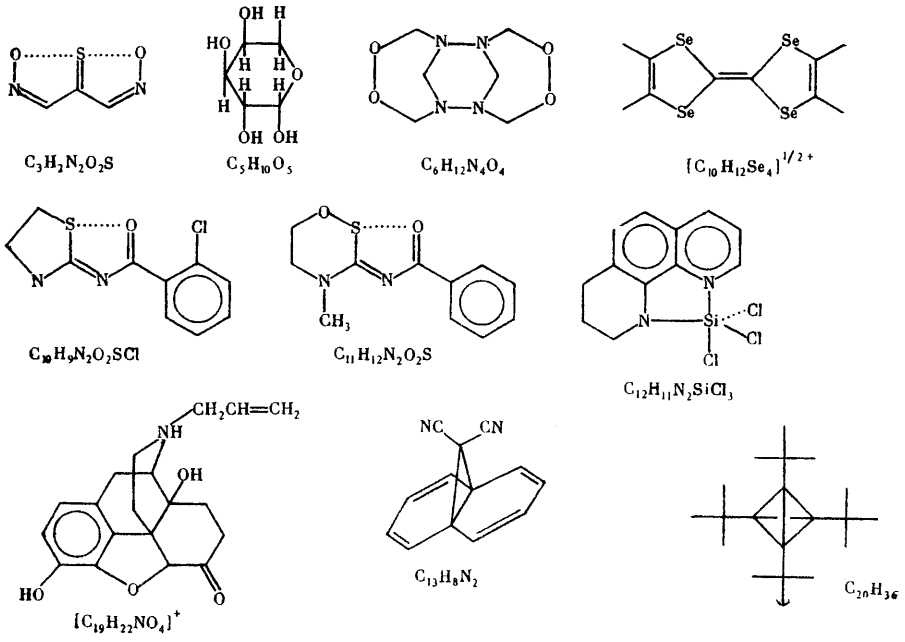


Figure 2. Structural formulae in Table 1.

motion.[21,37] Thirdly, as regards bond strength, the comparison of the deformation densities on bonds of this type (for example, O–O and N–N) is known *a priori* to be incorrect.[87]

However, the differences between the values of $\delta\rho_{max}$ in a single molecule can indicate the non-equivalence of isotypical bonds, which has been confirmed both theoretically and experimentally. For example, in the case of 9-t-butylanthracene $C_{18}H_{18}$, the values of $\delta\rho_{max}$ are approximately proportional to the overlap populations[10] calculated with the aid of the extended Hückel method. The extremely small value of $\delta\rho_{max}$ on the elongated C–C bridge bond in the compound $C_{13}H_8N_2$ [45] indicates that this is the weakest bond in the molecule. This conclusion is fully confirmed by chemical properties.

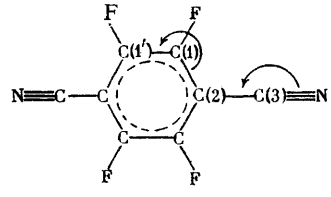
In certain cases, $\delta\rho_{max}$ proved to be smaller than the background level; one then speaks of the absence of a peak on the bond. The bond between inverted carbon atoms in the propellane derivative $C_{17}H_{19}N$, having the normal length, has been examined as an example in a review.[6] Theory describes such a bond with the aid of sp^4-hybrid [sic] orbitals whose overlap is indeed small.[110]

The causes of the systematic absence of peaks on bonds of the C–F and O–O types as well as certain others[7] were indicated above in Section III. The splitting of the peak on bonds formed by a silicon atom (Si–Si,[26] Si–Cl,[102] and Si–C [108]) is sometimes also observed.

The form of the covalent bond peak

Single, double, and triple bonds differ, apart from the values of $\delta\rho_{max}$, by the form of the equal deformation density surfaces. In the ideal case, single and triple bonds are manifested as peaks having the shape of ellipsoids of rotation (the axis of rotation is extended along the bond axis) with different ratios of the longitudinal and transverse half-axes.[111] The peak of the double bond in ethylene is extended at right angles to the plane of the molecule.[112] When single and multiple bonds alternate in the molecule, conjugation arises: the density of π-electrons is displaced from the multiple to the single bond (the mesomeric effect is designated in the structural formula by a curved arrow). This is reflected in the shape of the deformation density peaks.

A characteristic example is provided by tetrafluoroterephthalodinitrile $C_8N_2F_4$:[30]



The form of the peaks due to different bonds on the 0.1 e Å^{-3} multipolar pseudostatic δρ distribution surface is characterised by the following values (in Å).

	C(1')—C(1)	C(1)—C(2)	C(2)—C(3)	C(3)—N
Maximum width in the molecular plane (d_1)	0.89	0.89	0.93	1.30
Maximum width at right angles to the plane (d_2)	1.41	1.28	1.02	1.23
Bond length	1.38	1.40	1.43	1.15

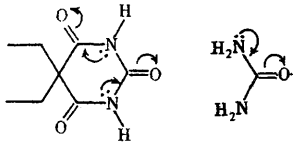
The sizes of the peaks confirm the existing ideas about the mesomeric effect and show that the π character of the bonds diminishes monotonically in the sequence C(1')–C(1), C(1)–C(2), C(2)–C(3), since the quantity d_2/d_1 diminishes (the latter is confirmed also by the increase in bond length). This means that the structure of the six-membered ring approaches the quinonoid structure, while the linear C(2)C(3)N fragment approaches the

cumulene type. We may note that the dynamic δρ distribution does not exhibit the quantitative features described. The existence of the inductive effect (transfer of electron density from C to F atoms and from the C atom to the N atom) follows from the atomic charges: F 0.13 e; C(1) 0.13 e; C(2) 0.05 e; C(3) 0.11 e; N 0.15 e.

The alternation of charges in a chain of four carbon atoms, which agrees with the ideas about the inductive effect, has been discovered also in the molecule of barbital $C_8H_{12}N_2O_3$.[113]

Polar bonds exhibit asymmetry in the δρ peak relative to the centre of the A–X internuclear section. For single bonds, having no π-component, the following regular feature is observed. If the bond polarity, measured by the quantity $\Delta q_{AX} = q_A - q_X$ (where q is the atomic charge) is large (of the order of 1 e), the δρ maximum is displaced towards the nucleus of the electronegative atom X, the function δρ diminishing faster in the direction of the X nucleus than in the opposite direction.‡ In organic molecules, purely single and at the same time polar bonds are encountered rarely; there are virtually no such bonds among organic substances for which carefully constructed δρ maps exist, (only in this case is there any point in discussing such fine details). Therefore examples of the features described can be more easily found among inorganic substances (the B–N bond in the cubic BN,[115] the Si–O bond in coesite,[116] and the Te–Cl bond in $C_2H_2TeCl_2$ [81]). Weakly polar bonds (for example, N–O, C–N, and C–O in $C_6H_{12}N_4O_4$ [95]) do not exhibit such asymmetry.

The characteristic features of bonds with a definite contribution of the π-component can be clearly seen in relation to barbital $C_8H_{12}N_2O_3$.[116] A shift of the charge on the C–N and C–O bonds in the π-region towards N and O bonds and in the plane of the molecule towards C bonds is observed in this instance. In the π-region, a similar feature, confirmed by theoretical calculations, is shown also by the carbonyl group in the urea CH_4N_2O molecule. Such behaviour of the π-charge can be explained by the schematic illustration of the mesomeric shift of electrons:



Hence it is clear that the population of the p_π orbitals of the N and O atoms is greater than unity and that of the C atom does not exceed unity. The differences between the orbital populations induce the asymmetry of the δρ peaks in the π-region. As regards the σ-charge, the example of parabanic acid $C_3H_2N_2O_3$,[47] two investigations of which led to completely different forms of the δρ peak in the σ-region of the C–N bond, makes it necessary to exercise caution in drawing inferences about the shape of the multiple bond peak in the molecular plane.

The asymmetry of the δρ peak for non-equivalent N–Si bonds in the compound $C_{12}H_{11}N_2SiCl_3$ [102] with a trigonal-bipyramidal coordination of the Si atom is manifested in different ways (Fig. 3). On the N_e–Si bond with an equatorially coordinated nitrogen atom, an appreciable displacement of the σ-density towards the Si atom and of the π-density towards the N_e atom is observed. The long bond with the axially coordinated nitrogen atom ($N_a \rightarrow Si$), which is formed by a donor–acceptor mechanism, exhibits different features. Its σ-component is displaced from the centre to the N_a atom and the π-component is virtually absent. Similarly to the single bonds discussed above, the quantity δρ diminishes in this instance from the maximum towards the N_a atom much more steeply than in the opposite direction.

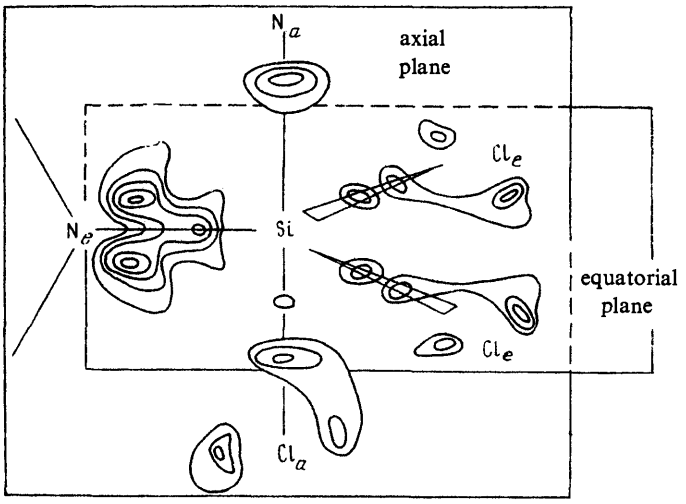


Figure 3. Schematic representation of the distribution of the deformation electron density in the SiN_2Cl_3 system.

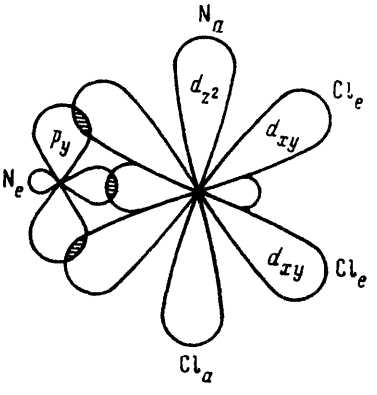


Figure 4. Interpretation of the electronic structure of the SiN_2Cl_3 system with the aid of atomic orbitals.

These facts can be explained with the aid of simple orbital ideas (Fig. 4). In the equatorial plane, the Si atom forms with the aid of sp^2-hybrid orbitals three σ-bonds (with the N_e atom and two Cl atoms). The N_e atom donates the electron pair occupying the p_y

‡We may note that the shift of the symmetrical peak to one of the nuclei can be induced not [only] by the bond polarity but by the difference between the sizes of the principal atomic regions (an example is provided by the C–S bond in the thiazolidine ring[114]).

orbital to the unoccupied d_{xy} orbital of the Si atom and forms a π-bond. The bond with the axial Cl atom is produced by the p_z orbital of the Si atom and the LEP of the N_a atom is transferred to the unoccupied d_{z^2} orbital. The extent of the atomic 3*d* orbitals in space explains the large distances from the Si nucleus to the peaks of the donor–acceptor bonds.

We may note that non-equivalence of the axial bonds is observed also in the trigonal-bipyramidal phosphorus compound C_2Cl_9P.[83]

The position of the covalent bond peak

In sterically strained systems, the δρ peaks deviate significantly from the bond lines in order to compensate for the decrease in the bond angle compared with the angle between the hybrid orbitals.[6]

The δρ map in the plane of the cyclopropane ring has been incorporated in textbooks and has become the classical image of banana bonds.[117] Another example is the cyclobutadiene fragment of the $C_{22}H_{32}S_2$ molecule, in which the following features of the δρ distributions have been observed.[118] In the plane passing at right angles through the centre of the C=C bond, there is in this instance a two-humped peak and the saddle section of the peak, corresponding to the σ-component, is further away from the ring axis than the maxima corresponding to π-electrons; for a single bond, δρ is close to zero at the analogously located points (at the same distances from the plane of the ring where the double bond gives rise to δρ maxima). The observed picture can be explained as a result of the superposition of distributions characteristic of a bent σ-bond and the usual π-bond, but non-empirical quantum-chemical calculation, performed for cyclobutadiene, did not lead to the observation of the double-humped peak described.

In compounds with electron-deficient bonds, a trend has been noted towards a shift of the δρ peaks into the inner region of the angle between such bonds.[119] Under these conditions the peaks fuse or a bridge is formed between them. Apart from inorganic compounds (metals, oxides) such features are observed in carbaboranes[120] and other boron compounds. Theory describes these compounds with the aid of three-centre two-electron orbitals localised at the centre of a three-membered ring made up of boron atoms.

Peaks in the region of unshared electron pairs

The height and shape of such peaks depend on the type of atom, its valence state, and the immediate environment.[6] Non-valence interactions or conjugation with π-bonds usually greatly influence the LEP peaks.

The N(III) atom has a single LEP. The corresponding δρ peak is manifested most clearly in the case of *sp*-hybridisation in the $-C\equiv N:$ group (for example, in $C_8N_2F_4$ [30]). The LEP of the angular dicoordinate nitrogen, occupying an sp^2-hybrid orbital, is also clearly manifested, for example, in the $C=\ddot{N}-C$ group (4-methylpyridine C_6H_7N [92]) and the $C=\ddot{N}-O$ group ($C_2H_6N_2O_2$ [80]). However, in the case of nitrogen with a planar ternary coordination, where the LEP occupies a *p* orbital, the maximum in the non-valence region is absent or is weak (in diformylhydrazine,[121] acetamide,[122] etc.). This is associated with the delocalisation of electrons on conjugation with double bonds. In the case of pyramidal coordination (in the compounds $C_6H_{12}N_4O_4$ [95] and C_3H_9N [86]), a diffuse LEP peak, occupying an sp^3 hybrid orbital, is observed near the N atom.

The two LEP of the oxygen atom give rise to two peaks located at an angle of ~130° in the case of sp^2-hybridisation. For sp^3-hybridisation, these LEP are usually manifested as a single longish peak (which agrees with non-empirical calculations for the H_2O molecule), but the intermolecular interactions sometimes lead to the splitting of this peak into two components. Numerous examples have been discussed in a review.[6] Here we shall only note that the peak corresponding to a single LEP can also be split, as has been observed for TeO_2.[123]

The remaining heteroatoms have been less thoroughly investigated. The unshared electron pairs of sulphur(II) usually behave like the oxygen LEP, but sometimes the height of their peak is comparable to the error of the determination of the δρ.[6] In the pyramidal SO_3^{2-} ion, the single LEP of sulphur(IV) has been observed at the apex of the pyramid.[124] The LEP peaks of the halogen atoms X (X = F, Cl) are manifested by a torus, whose axis coincides with A–X bond line and whose centre is displaced towards the A atom.[83,94,102] More rarely they appear in the form of three lobes directed at right angles to this axis.[89] Furthermore, there are negative minima in the direction opposite to the A–X bond line indicating the participation of the p_σ orbital of the atom X in the formation of this bond. A minimum is also observed on the C–F bond itself.[30,97]

Characteristic features of δρ in the region of hydrogen bonds

It was noted previously[6] that the δρ distribution along strong hydrogen bonds is approximately symmetrical relative to the midpoint despite the differences between O–H and O...H distances, while in the case of weak and moderately strong hydrogen bonds the δρ distributions are close to the superposition of δρ fragments.

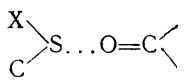
However, in a more detailed analysis of strong N–H...N interactions, it was noted[102] that the δρ distributions along the N...H bond and along the covalent N–H bond[89] differ somewhat. In the former case, the δρ peak is polarised (it descends gently) in the direction of the H atom, while in the latter case it is polarised in the direction of the N atom. It has also been noted that the steepness of the peak of the LEP not involved in the intermolecular interaction is approximately the same on the side of the nucleus and on the opposite side. The polarisation of this peak indicates a weak hydrogen bond. The specific C–H...N interactions in the 1,2,3-triazine crystal were in fact discovered on the basis of this feature[10] (*a priori* the appearance of such hydrogen bond was regarded as unlikely).

The redistribution of δρ on formation of hydrogen bonds has been frequently studied theoretically. Comparison of non-empirical calculations for the H_2O molecule in a free state and in a cluster, modelling the unit cell, indicates[125] an increase in the polarity of the O–H bonds and the transfer of electron density from the LEP and the hydrogen atoms to the O atom. On the other hand, the presence of short contacts (the formation of strong hydrogen bonds) increases the LEP peak. In the presence of several nearest neighbours, the changes in δρ are superimposed. For this reason, an increase in the number of neighbours blurs the characteristic features of the δρ distribution.

Thus according to the data presented, the idea that the δρ in weak and moderately strong hydrogen bonds is the sum of the deformation density of the LEP and the covalently bound hydrogen appears to be fairly approximate.

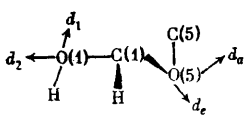
Redistributions of δρ induced by specific non-valence interactions

As an example of the influence of non-valence interactions on δρ, we shall present the results of a study[94] in which the intramolecular



interactions in the $C_{10}H_9N_2OSCl$ and $C_{11}H_{12}N_2O_2S$ molecules were compared (the lengths of the S...O contacts are 2.68 and 2.52 Å respectively). In the former case, two peaks of the LEP of the carbonyl O atom can be seen in the δρ distribution, while the peaks near the S atom are absent. In the latter case, the peaks due to the LEP of oxygen have almost completely vanished, while the S atom is surrounded by an intense δρ halo. Model calculations carried out with the aid of the extended Hückel method have shown that the order (covalence) of the bond between the atoms involved in these contacts reaches 4 and 25% respectively (compared with the covalent S–O bond).§ This can be explained by the fact that the interaction of the LEP of the O atom and of the antibonding molecular orbital of the S–X bond intensifies with increase in the electronegativity of the atom X.

Yet another example of specific non-valence interactions is provided by the anomeric effect in β-DL-arabinose,[15] which has been detected in the molecular fragment



where the letters *d* denote the LEP. It was established that the heights of the δρ peaks, corresponding to the unshared electron pairs d_a, d_e and d_2 are similar. For the d_1 pair, this quantity is smaller, because this LEP interacts with the C(1)–O(5) bond. It has also been noted that the δρ peaks on the "anomeric" C(5)–O(5) and O(1)–H bonds are significantly lower than on other bonds.

Manifestations of intermolecular specific non-valence interactions have been observed[81] in $(CH_3)_2TeCl_2$ crystals. Here the orbital of one molecule, occupied by the unshared pair of the Cl atom, interacts with the antibonding orbital of the Te–C bond of another molecule, which increases the level of δρ on the Te...Cl section.

From the standpoint of δρ distributions, the non-specific intermolecular interactions in organic crystals have so far been scarcely investigated. The effects associated with them are found at the limits of accuracy of the precision X-ray diffraction analysis but non-empirical quantum-chemical study of the intermolecular forces appears even more complex. It is therefore possible that new results, of fundamental importance for the theory of the structure of molecular condensed phases, will in fact be obtained in this precise region.

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¶ Non-empirical calculations for similar systems[126] yield similar results (10–30% covalence) only when the *d* orbitals of the S atom are included in the basis set.

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Low-temperature X-ray diffraction analysis: possibilities in the solution of chemical problems

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ABSTRACT. The possibilities of the modern precision X-ray diffraction method for the determination of the exact geometry, the characteristics of the thermal vibrations, and the distribution of electron density in the crystals of molecular compounds are examined in relation to a number of examples. The role of such investigations in the solution of chemical problems is demonstrated.

The bibliography includes 134 references.

Contents

I. Introduction 607
II. Determination of the exact molecular geometry 608
III. Analysis of atomic thermal parameters 611
IV. Study of the distribution of electron density in crystals 616

I. Introduction

The development of the X-ray diffraction method for the investigation of the structures of single crystals has been marked in recent years by a significant acceleration and simplification of the procedure used to obtain experimental diffraction data and to elucidate and refine crystal structures. At the same time there has been considerable growth also in the analytical possibilities of the method, which has proved extremely important for the actual solution of many chemical problems. In particular, use of low-temperature recording during a diffraction experiment (T < 100–150 K) made it possible to establish the structures of many fundamentally important simplest low melting and/or thermally labile compounds, including chemically unstable intermediates in chemical reactions,[1–3] which significantly extended the scope of X-ray diffraction analysis.

Acceleration of the measurement of structural data and the extension of the analytical scope of the method and in a certain sense of its routine applications (this includes low-temperature experiments) proved possible by virtue of the development of modern automatic diffractometers with appropriate attachments and highly effective sets of programs for crystal structures calculations on latest generation computers. The considerable increase in the number of structural studies throughout the world on molecular carbon-containing compounds is indicated, in particular, by the fact that the Cambridge Structural Data Centre contains at present information about the structures of more than 73,000 compounds[4] and the Centre receives annually approximately 6000–7000 new structures. Thus X-ray diffraction analysis has become one of the most important and useful methods for the study of structure in modern chemistry.

On the other hand, there has been an appreciable growth in recent years also in the real accuracy of the X-ray diffraction method. This has made it possible to extract from its results information of a new type, namely one can now establish detailed features of the steric structures of molecules and crystals, to discover the characteristics of atomic thermal vibrations, and also to investigate experimentally the distribution of electron density in crystals. In particular, the attainment of a precision in the determination of interatomic distances to within 0.002–0.003 Å permits a reliable detection of different electronic effects in molecules (the anomeric effect, the presence and absence of conjugation, etc.), which alter their geometry.

We emphasise that the standard errors in the interatomic distances obtained on refining crystal structures by the least squares method (LSM) fairly often have similar values. However, in the usual ("routine") experiments a whole series of factors (absorption, extinction, and diffuse scattering of X-rays, the asphericity of the electron distribution of atoms, the librations of the molecules and atomic groups in the crystals, the possible types of disorder, etc.) are not as a rule taken into account. These can introduce errors into the structural, including geometrical, parameters, which can sometimes be several times greater than the standard errors of the LSM. The correct allowance for these factors or reduction of their influence and hence the determination of the most reliable and accurate diffraction data and structural characteristics of the molecules and crystals is the task for modern precision X-ray diffraction analysis which has greatly developed in recent years.[5,6]

In the case of molecular crystals, which include almost all the crystals of organic, organoelement and organometallic compounds, one of the main and in many cases the principal condition governing the measurement of precise diffraction data involves the use of low temperatures (T < 100–150 K)† in X-ray diffraction experiments.[7] The increase in the accuracy of the X-ray diffraction analysis on reducing the temperature is mainly associated with the decrease in the amplitudes of atomic vibrations. The decrease in these amplitudes leads to a sharp rise in the intensities of the diffraction maxima, which permits in practice their measurement with a high statistical accuracy. On cooling molecular crystals to the

† In the vast majority of low-temperature devices, cold nitrogen vapour is used as the cooling agent (T_b = 77 K). X-Ray diffraction studies at helium temperature have so far been few in number (see, for example, Henriksen et al.[8]) in view of the complexity of the corresponding devices.

temperatures indicated, the greatest increase in the intensity of the large angle of reflections ($\sin\theta/\lambda > 0.6-0.7$ Å^{-1}) takes place. They are in fact largely determined by the scattering of X-rays by the electrons of the inner shells of the atoms, which are little perturbed on formation of chemical bonds and therefore the inclusion of such reflections in the LSM refinement of structures is extremely important and leads to the measurement of more correct thermal and positional parameters of atoms which have not been displaced as a result of chemical bonding effects. Such effects can incidentally be considerable for crystals made up of molecules containing multiple bonds of the type C≡C or C≡N. The refinement of structures of this kind only on the basis of "near" reflections, which is frequently the case when the experiments are carried out at room temperature where "far" reflections are absent due to intense thermal vibrations, can lead to a systematic shortening of such bonds by 0.01 Å and more, although the error, determined by the LSM, in the interatomic distances can be almost an order of magnitude smaller.[9]

At low temperatures, where the possibility of a reliable measurement of large angle reflections arises, it is possible to avoid this source of systematic error as a result of the appreciable increase in the contribution of such reflections to the X-ray scattering, which corresponds to a large extent to scattering by spherically symmetrical atoms—this is one of the main approximations in the X-ray diffraction analysis. The cooling of crystals and the associated decrease in the atomic vibration amplitude lead also to a decrease in a series of other effects (anharmonicity, diffuse thermal scattering, the "freezing out" of certain low-frequency vibrations), which also affect the thermal and geometrical parameters. Furthermore, on cooling, there is an increase in the radiation and chemical stabilities of the crystals. In particular, in the case of molecular crystals, a decrease in temperature to 100–150 K decreases the librations of the molecules or their fragments in crystals as a whole and hence there is an appreciable decrease in the so called "librational" shortening of bonds—an effect attaining 0.02–0.03 Å at ~300 K. On the other hand, the introduction into the diffraction data obtained at the usual temperature of corrections applied to the bond length is not always effective, because the corresponding mathematical models, used in the structural analysis for the description of thermal movements and for the calculation of these corrections,[10] are frequently themselves correct only at low temperatures (since they are based on the small displacement approximation). In addition, it is evident that in many cases the determination from X-ray diffraction data (for molecular crystals) of correct values of the parameters of the anisotropic thermal vibrations (more precisely the mean square displacements) of the atoms is in many cases possible only at low temperatures.[11,12] The progress achieved in recent years in the determination of physically significant parameters of atomic mean square displacements or thermal ellipsoids and the development of methods for the theoretical calculation of these parameters[13,14] and of different criteria of their reliability[15,16] have made possible the extraction from the results of the precision X-ray diffraction experiment of additional new information associated in particular with the determination of the types and energy characteristics of different intramolecular movements in crystals (including movements due to the conformational changes in the molecules) and with the study of the nature of the disorder and phase transitions.

The possibility of obtaining accurate X-ray diffraction data, characterised by the accuracy of the determination of the correct set of kinematic structural amplitudes to within ~1–2% makes it possible to find from the experimental X-ray diffraction data the electron density distribution function for the crystal $\rho(r)$.[17–19] It is important to emphasise that this function defines uniquely the structure and physicochemical properties of the test system (the Hohenberg–Kohn theorem[20]). The latter factor provides a basis for the formulation in the language of electron distribution of various chemical problems (together with other problems), the most important of which involves the establishment of the nature of the chemical bond in compounds of different classes. Here too the experimental determination and visualisation of the characteristic features of the function $\rho(r)$, for example, in the form of electron density distribution maps, makes it possible to obtain valuable information about the nature of the chemical interaction and reactivity of molecules.

The method most widely used in such investigations involves the construction and analysis of maps of the so called deformation electron density (DED), defined as the difference $\delta\rho(r) = \rho(r) - \rho^0(r)$, where $\rho(r)$ is the total electron density of the crystal derived from the experiment, while $\rho^0(r)$ is the calculated electron density of spherically symmetrical non-interacting atoms (of the "premolecule"). The function $\delta\rho(r)$ thus describes the character of the redistribution of electron density on formation of chemical bonds between the initially non-interacting atoms, i.e. permits the "visualisation" of the formation of such bonds. It is significant that DEP maps can be constructed from the results of the X-ray diffraction experiment alone, while the quantity $\rho^0(r)$ can be calculated from the results of the large angle refinement of structures by the least squares method (the so called "$X-X$" method for the construction of DED maps). Bearing in mind that the function $\delta\rho(r)$ generally represents a small difference between two large quantities $\rho(r)$ and $\rho^0(r)$, the experimental determination and calculation of the latter should be carried out with a high accuracy, which can be achieved for molecular crystals in most cases only by using low temperatures and by applying the corrections listed above (for absorption, extinction, etc.) to the diffraction data obtained. This review deals with certain examples of the results of precision (low-temperature) X-ray diffraction analysis for the solution of various chemical problems, mainly associated with the determination of the accurate geometry of the molecules and of the detailed features of the steric structure and the characteristics of thermal vibrations in molecular crystals and also with the establishment of the character of the distribution of electron density.

The review does not consider methodological questions involving the employment and application of various low-temperature devices in X-ray diffraction experiments (such devices have already been considered[7,21]) as well as questions associated with the use of low temperatures for the investigation of low melting and/or metastable compounds (other reviews[1,22] have been devoted to these problems). The principal task of this review is the elucidation and consideration, in relation to a number of examples, of the potential of the method associated with its increasing true accuracy in the low-temperature study of crystals of molecular compounds.

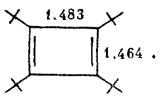
II. Determination of the exact molecular geometry

We shall consider certain examples of studies of molecular crystals carried out in order to obtain the exact molecular geometry (with an error of the determination of the interatomic distances between non-hydrogen atoms in the range 0.001–0.003 Å) from diffraction data.

Such studies are extremely important for the development of modern structural chemistry, since they permit a reliable determination of very detailed and in many instances fundamentally important features of the structures of molecules and crystals. As already mentioned, the use of low temperatures is one of the main conditions for the determination of accurate structural results, because it is then possible to measure a sufficient number of "large angle" reflections.

In particular, a recent low-temperature (123 K) study[23] of tolane Ph−C≡C−Ph established that the length of the C≡C triple bond is 1.211(2) Å according to the results of the large angle refinement ($\sin\theta/\lambda > 0.65$ Å^{-1}), whereas refinement of the structure only in terms of the near reflections, which is equivalent to the employment in the experiment of Cu radiation for which $\sin\theta/\lambda < 0.65$ Å^{-1}, yielded a significantly smaller length of this bond: 1.196(2) Å. Thus the effective shortening of the triple bond in the usual experiment is by 0.015 Å for tolane, which is comparable or can even be greater than the real change in the length of this bond due to the electronic conjugation effects.

An X-ray diffraction study of tetra(t-butyl)cyclobutadiene (I) at room temperature[24] showed that the central ring has a nearly square planar geometry.



(I)

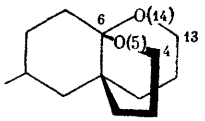
This conflicted with many other experimental (including X-ray diffraction) and calculated data and forced the authors to postulate the presence of dynamic or static disorder in the crystal of compound (I), leading to the superposition of two orientations of the central rectangular (and not square) ring, differing by a rotation in the plane by 90°. A reinvestigation of compound (I) at 123 K [25] confirmed the existence of such disorder and its diminution at a low temperature led to a decrease in the contribution of the alternative form to 15−30%, which made it possible, in its turn, to establish more correct bond lengths in the ring [1.441(2) and 1.527(2) Å; for other known cyclobutadiene derivatives in which there is no disorder the corresponding distances are 1.34 and 1.60 Å]. We may note that the partial disorder in the molecule of compound (I) at low temperatures can be clearly discovered by means of a detailed analysis of the parameters of atomic thermal displacement (see below).

Other examples are associated with the study of the geometry of arene or other π-complexes of transition metals with cyclic polyene ligands. Quantum-chemical calculations have shown[26] that in the case of such π-complexes of the type $(\eta^n\text{-}C_nH_n)M(CO)_m(XY)$ (n = 3−7, m = 1−3, XY = CO, N_2, NO, CN, M = transition metal) the electronic influence of the metal should reduce the symmetry of the coordinated η^n-cyclic ligand and should give rise to a characteristic change in its geometry. In particular, the alternation of the C−C bond lengths in the benzene ring should be observed for η^6-arene complexes.

Indeed, the alternation of C−C bonds in a six-membered ring was observed in a low-temperature study (77 K) of benzenechromium tricarbonyl $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ the C−C bond eclipsed by CO groups are lengthened compared with the other bonds in the ring by 0.017(2) Å. This small change in molecular geometry is correlated with the characteristics of the electron distribution maps near the Cr atom.[28] Subsequently the effect was confirmed[29] also in a low-temperature diffraction study of similar complexes $(\eta^6\text{-}C_6Me_6)Cr(CO)_3$ [Δ = 0.021(4) Å] and $(\eta^6\text{-}C_6Me_6)Mo(CO)_3$ [Δ = 0.036(9) Å]. However, we emphasise that, as a consequence of the considerable librations of η^6-linked rings at room temperature, this extremely fine electronic effect, which is of fundamental importance for the understanding of the nature of the chemical bond in transition metal π-complexes, could not be recorded experimentally in any of the three compounds indicated.

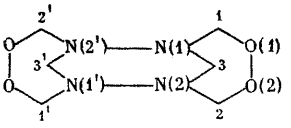
The effects associated with the manifestation of the so called orbital n,σ^*-interactions belong to the class of important stereoelectronic effects which determine to a large extent the characteristic features of the structure and reactivity of certain molecules of organic and organoelement compounds.[30] Interactions of this type can affect also the geometrical characteristics of the molecules. In particular, according to the results of quantum-chemical calculations for methanediol and methoxymethanol[31,32] in the synclinal (*sc*) and antiperiplanar (*ap*) conformations, the C−O bonds located in the *ap*-position relative to the lone electron pairs (LP) of the O atoms are lengthened relative to the other C−O bonds by 0.025−0.030 Å.

The reliable detection of small geometrical effects of n,σ^*-interactions becomes possible in highly accurate low-temperature X-ray diffraction studies. In particular, the O(5) and O(14) oxygen atoms in the structure of dihydroxypropellane ketal (II), investigated[33] at 98 K, are chemically equivalent but conformationally different: the C(6)−O(14) bond has the *sc*-orientation relative to the O(5)−C(4) bond and hence the *ap*-orientation relative to the LP of the O(5) atom; on the other hand, the C(6)−O(5) bond is characterised by the *ap*-orientation relative to the O(14)−C(13) bond and by the *sc*-orientation relative to the LP of the O(14) atom.



(II)

As a consequence of the different effectiveness of the orbital n,σ^*-interactions, the difference between the C−O bond lengths in the molecule of compound (II) is 0.026(3) Å [C(6)−O(5) = 1.412 Å, C(6)−O(14) = 1.438 Å]. A similar difference between the lengths of the chemically equivalent C(1)−N(1) and C(2)−N(2) bonds (0.025 Å) and between the C(1)−O(1) and C(2)−O(2) bonds (0.017 Å) has been observed in a study of the tricyclic compound (III) (data obtained[34] at 96 K), which is also induced by the different effectiveness of the interaction of the LP of the N(1) and N(2) atoms with the σ* orbitals of the C−O bonds:



(III)

The use of low temperatures gives rise to the possibility of investigating the manifestation of such stereoelectronic effects in crystals of the simplest molecular compounds which are in many instances liquid with low melting points or gases. The methodological questions involving the preparation of single crystals of low-melting compounds from liquids (melts) having melting points ranging from room temperature to about −150 °C needed for studies of this kind have been examined in a number of reviews[1,7,22] and will not be discussed here. We may note only that data on the structures of such usually very simple compounds are of special

interest for structural chemistry: they can be used to investigate the characteristic features of the steric structure of molecules (for example, the geometrical manifestation of various electronic effects) and crystals (the specific features of intermolecular interactions) in a "pure" form, i.e. in those cases where the molecules lack different functional substituents, which, on the one hand, enable the compounds to form crystals stable under the usual conditions, but, on the other hand, influence those properties of the test molecules which are difficult to determine beforehand.

As an example, we shall present data obtained in a recent study of the molecular structure of dimethoxyamine $HN(OMe)_2$ (IV) [35] and tetramethoxyhydrazine $(MeO)_2N-N(OMe)_2$ (V) [36]—the simplest (and low melting) alkoxyamines in which n,σ^*-interactions play an important role according to the available chemical data. The molecular structures of compounds (IV) and (V) and their principal geometrical parameters are presented in Figs. 1*a* and 1*b*.

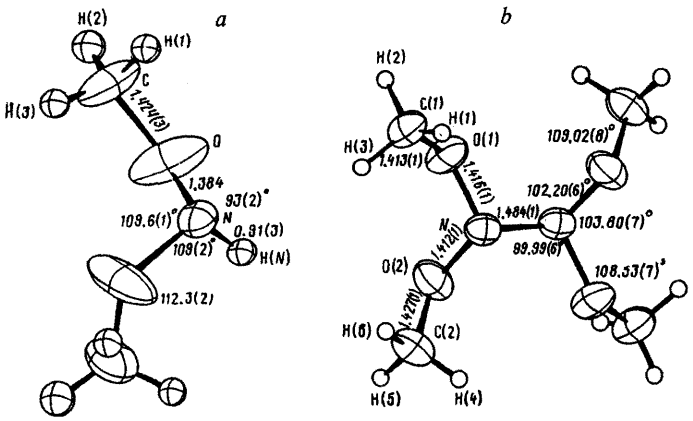


Figure 1. The crystal structure and principal geometrical parameters of the molecules of dimethoxyamine (IV) (*a*) and tetramethoxyhydrazine (V) (*b*).

It has been established that in the crystal of compound (IV) the molecules have a conformation characterised by a CONO torsional angle of 78.7°; the Me groups are then displaced from the ONO plane on either side. Electron diffraction study of this compound in the gas phase and the results of electrooptical measurements in solution established that mainly this conformation of the molecule is retained in the free state and in solution.[35] The preferred retention of this conformation is apparently determined by the fact that it is optimal for the occurrence of the stabilising $n_O-\sigma^*_{NO}$ interaction, as a result of which the N–O bond length in dimethoxyamine is reduced to 1.384(2) Å compared, for example, with 1.496(9) Å in MeO–NH(Me), where there is no such possibility. On the other hand, in the case of tetramethoxyhydrazine (V) (centrosymmetrical molecule, CONO torsional angles of 108° and −132°), the effectiveness of this interaction is smaller than in dimethoxyamine, which lengthens the N–O bonds to 1.414(2) Å. On the other hand, the conformation of compound (V) is favourable for the occurrence of another stabilising interaction of the type $n_O-\sigma^*_{N-N}$ whose occurrence is manifested by the lengthening of the N–N bond in this compound by 0.038 Å compared with hydrazine. It has been noted[37] that the ready homolysis of the N–N bond is a chemical manifestation of this electronic effect.

The interesting question of the relation between the reactivity of molecules, for example, their capacity to undergo dissociation at specific bonds, and the length of such bonds (in the ground electronic state) arises in this instance. A series of studies have been devoted to such questions.[38–42]

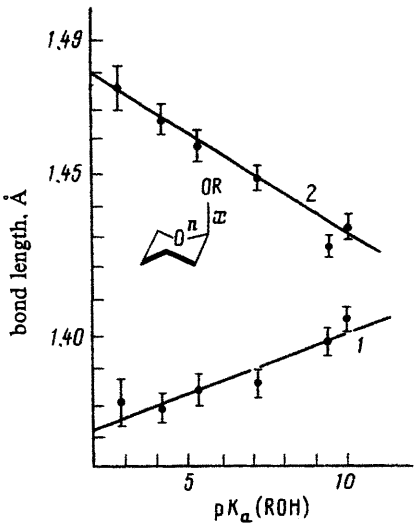


Figure 2. Dependence of the C–O bond lengths in a series of aryl derivatives of tetrahydropyranyl acetals on the pK_a for the corresponding acids ROH:[39] *1*, *n*; *2*, *x*.

For example, structural and kinetic studies of a series of aryl derivatives of axial tetrahydropyranyl acetals established a linear correlation between the lengths of the endocyclic and exocyclic C–O and C–OAr bonds, on the one hand, and the pK_a of the corresponding conjugate acids ArOH (Fig. 2), on the other. According to Briggs et al.,[39] the pK_a determine the rate constants for the hydrolysis of the acetals, i.e. for the reactions involving the heterolytic dissociation of the C–OAr bond, and hence the free energy of activation. With increase in the effective electronegativity of the OAr substituent as a consequence of the increasing effectiveness of the $n_O-\sigma^*_{C-O}$ interaction, the endocyclic C–O bond is appreciably shortened and the axial C–OAr bond is lengthened, which increases the rate of hydrolysis. The profile of the coordinate of this reaction plotted from the experimental data using the method of structural correlations[41,42] made it possible to estimate the slope of the $\Delta E/\Delta r$ curve in the initial stage of the stretching of the C–OAr bond, which proved to be 260 ± 10 kcal mol^{-1} Å^{-1}. Thus the energy expended on the stretching of the bond of the type under consideration by ~0.01 Å is fairly large and amounts to ~3 kcal mol^{-1}, which necessitates the determination of the geometrical characteristics of the molecules with a high accuracy in studies of this kind. We may also note that, when stereoelectronic effects (for example the anomeric effect) in compounds containing elements of the Third Period (O, S, P) are considered, the corresponding effects of the substituents are much weaker. In particular, the energies and geometries of all the possible molecules of doubly substituted methanes XCH_2Y, in which the substituents X, Y = F, OH, NH_2, Cl, SH, or PH_2 contain elements of the

Second and Third Periods, have been calculated[43] by the SCF LCAO-MO method (in terms of the 3-21G* basis set). It was established that the energy of the interaction of the substituents Cl, SH, and PH_2 is significantly lower than for substituents containing the elements of the Second Period. The geometrical manifestation of these effects should also be apparently weaker; this requires an improved reliability of the structural data for their reliable identification.

III. Analysis of atomic thermal parameters

An important characteristic feature of the precision X-ray diffraction method is the possibility of extracting from diffraction data the correct values of atomic thermal parameters[6,7,9,11,16] or temperature factors.‡ Their analysis permits conclusions about the types and characteristics of the low-frequency motions and/or static atomic displacements occurring in the crystals.

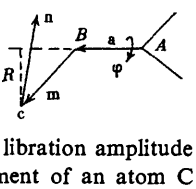
In the case of molecular crystals, such analysis is usually carried out within the framework of the familiar "rigid-body" model,[10] the essential feature of which consists in the separation of atomic vibrations into "external" low-frequency and "internal" high-frequency modes and in the neglect of the contribution of the latter to the temperature factors. Here it is also assumed that static displacements, induced, for example, by the disorder among the atoms in the crystals, are absent. Evidently, as a consequence of the smallness of their amplitude the contribution of the high-frequency vibrations to the temperature factor should be much smaller than that of the low-temperature frequency vibrations. For example, typical mean square amplitudes of the stretching vibrations in organic molecules are 0.001–0.002 Å^2 for non-hydrogen atoms,[44] which is in many cases smaller by an order of magnitude than the values calculated from the experimental temperature factors. As a result, the vibrations of molecules or the vibrations of their constituent components as a whole make the main contribution to the atomic temperature factors for crystals of molecular compounds.

In conformity with the "rigid-body" model considered,[10] the harmonic movement of molecules in the crystal as a whole can be described in the general case with the aid of three tensors: the translational (**T**), librational (**L**), and translational-librational (correlation) (**S**) tensors, containing 20 independent components. The mean square displacements of any atom, i.e. the components of its temperature factor in the harmonic approximation, represented in the form of the so called thermal ellipsoid, can then be expressed in terms of these tensors and also in terms of the equilibrium position of the atom in an explicit form. Thus the description of the thermal motion of a molecule in a crystal containing n independent atoms with the aid of $6n$ temperature parameters of the ellipsoids of thermal vibrations of each atom can be reduced to the consideration of only 20 components of the three **LTS** tensors. These components are determined by the least squares method either using as the "variables" the $6n$ already refined components $U_{ij}(B_{ij}, \beta_{ij})$ of individual temperature factors or by refining the LTS-tensors directly on the basis of diffraction data.[45]

The agreement between these parameters, obtained from diffraction data (U_{ij}^{exp}) and calculated on the basis of the hard body model (U_{ij}^{theor}) is a measure of the physical significance of the temperature parameters and of the suitability of the **LTS** model. Evidently, if the difference $\Delta U_{ij} = U_{ij}^{exp} - U_{ij}^{theor}$ is small and close to the error of the experimental determination $\sigma(U_{ij})$, the temperature parameters correspond to the rigid-body model within the limits of the accuracy attained.

However, it is evident that the model is too simplified and that the discrepancy between U_{ij}^{exp} and U_{ij}^{theor} should not always be understood merely as an indication of an experimental error in the determination of U_{ij}^{exp}. The slow low-frequency ($\omega \leqslant 500$ cm^{-1}) intramolecular vibrations, not taken into account in the **LTS** model, can introduce an appreciable contribution to the values of U_{ij} and the identification of such movements, which can be precursors of conformational transformations in crystals, is in fact of significant interest. Therefore, subsequently, after the appearance of the rigid-body model, other more complex versions of the description of the thermal motion of atoms and crystals were developed. In particular, they make it possible to take into account the non-rigidity of the molecular skeleton. One of the first attempts to take into account the intramolecular movements in the description of atomic thermal parameters was the "riding" model widely used for the description of the thermal movements of terminal atoms in molecules, especially hydrogen atoms.[46] Next, mention should be made of Johnson's model which has been called the "segmented rigid-body" model[47] and was subsequently developed for the description of the thermal motion of macromolecules,[48] and of the studies of Hamilton and co-workers[49] on the torsional oscillations of methyl groups in different organic molecules (on the basis of neutron diffraction data). A method has been proposed recently for analysing the thermal parameters in which it is possible to calculate the force constants of the slow intramolecular movement. It is based on the inclusion in the least squares procedure of the parameters of the quasi-normal modes of these movements together with the simultaneous refinement of the components of the **LTS** tensors.[50] The procedure has been tested successfully in the description of thermal motion in two lipid derivatives characterised by significant torsional librations about the single bonds linking the rigid cyclic molecular skeleton to the flexible aliphatic chains.

A fairly simple one-parameter model, in which together with the calculation of the corresponding **LTS** tensors there is a possibility of taking into account and calculating the amplitudes of intramolecular torsional vibrations, has been developed in recent years for practical applications in studies of this kind.[51,52] In this model, a single parameter φ (the libration amplitude) is introduced for each atom or group of atoms which can execute torsional vibrations about the given bond (for example, the vibrations of a C atom about an A–B bond).



$$\mathbf{n} = \mathbf{m} \times \mathbf{a} / |\mathbf{m} \times \mathbf{a}|;$$
$$R = |\mathbf{m} \times \mathbf{a}| / |\mathbf{a}|.$$

If the libration amplitude is not too great, it can be regarded as the movement of an atom C in the direction of a unit vector **n**. The additional displacement of the atom C as a result of such intramolecular movement is φR and this movement is superimposed on the displacement of the molecule in the crystal as a whole. The mean square amplitude $\langle\varphi^2\rangle$ as well as the components of the **LTS** tensors are refined by the least squares method. The model

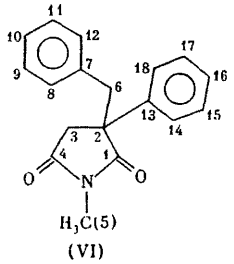
‡ It has recently become common usage to call these parameters the parameters of the mean square displacement amplitudes (the English abbreviation is MSDA), because not only atomic vibrations but also different kinds of static displacements of atoms from equilibrium positions contribute to the Debye–Waller factor (the "temperature" factor).

considered proved to be extremely efficient and suitable for the description of intramolecular movements in crystals with fairly large torsional amplitudes ($\varphi < 20-25°$).

However, in the general case, in the analysis and interpretation of the temperature parameters within the framework of the simple rigid-body LTS model or when its more complex versions are used, difficulties frequently arise which are both associated with the unduly high degree of simplification of the models and are purely mathematical.[53] Therefore, in the interpretation of the temperature parameters, the search for other criteria of their quality and reliability becomes important.

For molecular crystals, one of the ways of testing the quality of atomic thermal parameters and of discovering the types of intramolecular movements (or disorder) occurring in crystals involves the calculation of the differences Δ between the mean square amplitudes of the opposed vibrations of pairs of atoms in the direction of the chemical bond between them (the so called Hirshfeld test[15] of the "rigidity" of the bond: $\Delta_{AB} = Z^2_{AB} - Z^2_{BA}$, where Z^2 is the projection of the mean square vibration amplitudes of the atoms A and B onto the direction of the A–B bond in the compound investigated). If Δ_{AB} is small ($\lesssim 10^{-4}$ Å^2) for the given chemical bond between the atoms A and B in the molecule, which corresponds to significantly smaller amplitudes of the stretching vibrations of the atoms compared with the vibrations of the molecules in the crystal as a whole, then the thermal ellipsoids for the atoms A and B correctly reproduce the character of the atomic movement. On the other hand, if Δ is significantly greater than 10^{-4} Å^2, then some other additional atomic displacements apparently contribute to the thermal parameters of the atoms A and B or there is a systematic error in their calculation. For structurally rigid systems, for example for molecules with three-dimensional frameworks or for cyclic systems, with correctly determined thermal parameters, the values of Δ should be small also for all pairs of atoms not linked by valence bonds, confirming the rigidity of the entire molecular skeleton. However, if the test of the rigidity of chemical bonds is positive and the calculation of Δ for certain pairs of chemically non-bonded atoms in the molecule yields values of Δ much greater than 10^{-4} Å^2, this result can indicate the occurrence in the given molecule of definite types of intramolecular movements. Such calculation of the values of Δ has been frequently used recently to elucidate the types of such movements.[16]

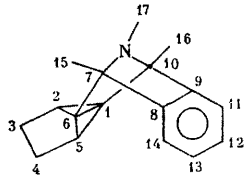
As one of the examples of the analysis of the values of Δ, we shall consider the result of the study of a crystal of 3-benzyl-*N*-methyl-3-phenylsuccinimide (VI) at 100 K:[54]



(VI)

The average value of Δ for all 23 pairs of chemically bonded atoms in compound (VI) is 21×10^{-4} Å^2, which is comparable to the values of $\sigma(\Delta) \simeq 15 \times 10^{-4}$ Å^2. The values of Δ for pairs of atoms linked by valence bonds in three fragments, namely the *N*-methylsuccinimide fragment (8 atoms), the benzyl fragment (7 atoms), and the phenyl fragment (6 atoms), are also small, amounting to 19, 24, and 11 ($\times 10^{-4}$ Å^2) respectively, which indicates their structural rigidity. On the other hand, calculation of the average values of Δ for pairs of non-bonded atoms belonging to different fragments indicates the non-rigidity of the molecular skeleton of compound (VI) as a whole: $\Delta = 71 \times 10^{-4}$ Å^2 (imide–benzyl), 38×10^{-4} Å^2 (imide–phenyl), and 44×10^{-4} Å^2 (benzyl–phenyl). This structural non-rigidity is probably due to the possibility of the torsional vibrations of the three rings relative to the C(2)–C(6), C(7)–C(6), and C(2)–C(13) single bonds of the central fragment of the molecule of compound (VI).

In the study of the structure of the [3.1.1]propellane derivative (VII), it was established (structural data for 95 K [55]) that, for all the pairs of chemically bonded atoms, the Hirshfeld test of the rigidity of the bonds is positive with a high degree of accuracy [$\Delta_{av} = 3(7) \times 10^{-4}$ Å^2], which indicates a high quality of the diffraction data. The molecule as a whole is also fairly rigid — the average value of Δ for all the pairs of atoms not linked by valence bonds [with the exception of pairs with participation of the C(17) atom of the methyl group attached to the N atom] is less than 10×10^{-4} Å^2.



(VII)

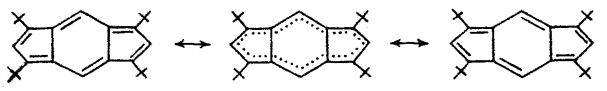
Calculation of the values of Δ for the non-bonded pairs of atoms with participation of the C(17) atom shows, however, that there is an appreciable movement of this atom relative to the C(8)–C(14) carbon atoms on the right-hand side of the molecule [displacement in the direction C(17)...C(8)–C(14)]. On the other hand, such additional countermovement has not been observed relative to the atoms in the left-hand part of the molecule [the C(1)–C(7), C(10), C(15), and C(16) atoms]:

	C(1)÷C(7), C(10), C(15), C(16)	C(8)	C(9)	C(11)	C(12)	C(13)	C(14)
Δ ($\times 10^4$ Å^2)	0–6	17	21	33	39	38	25

Thus the additional movement (detected in the thermal parameters of the structure) of the C(17) atom of the methyl group takes place along an arc around the nitrogen atom, i.e. it corresponds to the beginning of the possible route to the inversion of the configuration at this atom.

Calculation of the differences Δ for the same compound, investigated at different temperatures, makes it possible in a number of instances to establish the most readily "frozen out" types of intramolecular vibrations. In particular, a study[56] of the trigonal-bipyramidal phosphorane $Cl_3P(CCl_3)_2$ (VIII) at 153 K demonstrated the structural rigidity of the molecule: calculation of the differences Δ for all the chemically bonded and also non-bonded pairs of atoms at distances $\lesssim 3.2$ Å yields the mean square value $\Delta = 7 \times 10^{-4}$ Å^2. On the other hand, the analogous calculation using high-temperature data (300 K [57]) leads to $\Delta = 85 \times 10^{-4}$ Å^2; the pairs of atoms not linked by valence bonds and including atoms of only one of the two CCl_3 groups are characterised by the maximum values of Δ [$\Delta = (112-166) \times 10^{-4}$ Å^2]. This evidently indicates the additional libration of this group in the crystal, which was also detected from ^{35}Cl NQR data. The barrier to the rotation of this group, estimated from diffraction data, proved to be approximately 57 kJ mol^{-1}.[58] The possibility of the libration of only one of the two CCl_3 groups is due to their different environments in the crystal.

Naturally, it is difficult to establish the occurrence of a specific type of intramolecular movements (or the presence of disorder) in crystals by analysing only the values of Δ. However, calculation of Δ is a very simple and reliable criterion for discovering the presence of these effects. For example, in the study of the cyclobutadiene derivatives (I) at 123 K [25] already mentioned, the presence of residual ring disorder is manifested by the relatively large value of $\Delta_{C,C}$ (compared with other values) for the carbon atoms of the central ring ($\Delta_{C,C} = 19 \times 10^{-4}$ Å^2). On the other hand, the study of the structure of the derivative of S-indacene (IX) at room and low (100 K) temperatures showed[59] that the molecule in the crystal has the intrinsic D_{2h} symmetry of the carbocycle, which corresponds to the equalised structure (B) and agrees with ^{13}C NMR data:[60]



(IX, A) (IX, B) (IX, C)

Analysis of the differences $\Delta_{C,C}$ for the ring carbon atoms in the molecule of compound (IX) confirmed its structural rigidity ($<\Delta^2_{C,C}>^{1/2} = 7 \times 10^{-4}$ Å^2), which rules out the possibility of the coexistence of the valence isomers (A) and (C) in the crystal. This result forced the authors[59] to put forward the hypothesis that in the case under consideration there is a possibility either of the stabilisation in the crystal of the delocalised non-aromatic 12 π-electron system or the geometry of the molecule corresponds to the transition state of the valence isomerisation reaction stabilised by crystal packing.

In view of the foregoing, it appears useful to analyse the values of Δ for crystals of different tautomeric compounds and also for crystals of compounds with strong hydrogen bonds (for example, of the type O−H...O) and a central H atom. Such analysis makes it possible to discover the contribution to the structure observed in the crystal by possible "limiting" valence forms.

More important information about the intramolecular movements is obtained (which makes it possible to establish not only a qualitative but also a quantitative measure of such movements) using the one-parameter model discussed above,[51,52] on the basis of which it is possible to calculate the mean square amplitudes of the intramolecular torsional vibrations $<\varphi^2>$. Next, it is possible to calculate, using familiar formulae, the force constants f and other characteristics of such movements:[16,61]

$$f = kT/\langle\varphi^2\rangle. \quad (1)$$

Strictly speaking, in the calculation of the libration force constant ($f = 4\pi^2 I\nu^2$, where I is the moment of inertia and ν is the frequency in cm^{-1}), one should use a quantum-chemical expression for $<\varphi^2>$:

$$\langle\varphi^2\rangle = \frac{h}{8\pi^2 I\nu^2}\,\mathrm{Coth}\left(\frac{h\nu}{2kT}\right). \quad (2)$$

However, it has been shown[61] that Eqn. (2) reduces to the classical Eqn. (1) to within at least 1% for frequencies $\nu < 0.2\ T$ (ν is expressed in cm^{-1} and T in K), which is valid at normal temperatures for almost all groups except $-CH_2$, $-CH_3$, $-NH_2$, and $-NH_3$. Having specified the usual form of the rotational potential V [$V = B(1 - \cos n\varphi)/2$], where B is the height of the potential barrier, and having expanded V in series, we obtain

$$V = \frac{B}{2}[1 - (1 - n^2\varphi^2/2 + \ldots)] \simeq \frac{Bn^2\varphi^2}{4}. \quad (3)$$

Having set this expression equal to $V = f\varphi^2/2$, we have in the classical limit

$$B \simeq 2f/n^2 = 2kT/n^2\langle\varphi^2\rangle. \quad (4)$$

Thus, not only the frequencies and force constants but also the heights of the barriers to slow intramolecular vibrations in crystals can be estimated from the values of $<\varphi^2>$ determined from diffraction data. On the assumption that the selected form of the cosinusoidal potential is valid, Eqn. (4) proved to be sufficiently accurate (the error is less than 10%), provided that the height of the barrier B exceeds $12kT/n^2$,[61] i.e. provided that the mean square amplitude $<\varphi^2> < 0.17$ rad^2 ($\varphi < 25$ °C). The possible barriers B as well as the frequencies and force constants for more than 300 groups have been estimated[61] on the basis of the corresponding calculations of the quantity $<\varphi^2>$ from the experimental temperature parameters $U_{i,j}$ for 125 different structures of molecular crystals using data from the Cambridge Crystallographic Data Centre. Certain results, including those obtained recently,[58,62] are presented in Table 1, which shows that the calculated barriers fall within the range found by means of other methods. Such estimates may prove useful, particularly in the absence of the corresponding experimental data obtained by other methods (non-elastic scattering of neutrons, relaxation NMR methods, NQR spectroscopy, etc.), or in comparing the results obtained by different methods. In this connection, we may note the tabulated (Table 1) estimates of the barriers to the rotation of the cyclopentadienyl and permethylated cyclopentadienyl rings in metallocenes, for which a good agreement has been observed with the results found by NMR relaxation methods, as well as the data for the barriers to rotation in phosphazo-compounds, which agree with the studies of these compounds by the NQR method.

Table 1. The barriers to the intramolecular movements of certain atomic groups in crystals estimated from X-ray diffraction data.[58,61,62]

Group	Atom linked to group	Height of barrier, kJ mol^{-1}	
		calc. by Eqn. (4)	from data obtained by other methods
$-CH_3$*	Trigonal C, N Tetrahedral C, N, P O	B_3 = 1.5–9.6 B_3 = 4–26 (cf. Ref.11) B_3 = 1–9 (cf. Ref.4)	1.2–8.5 (crystal) 12–22 (gas) 4.5 (CH_3OH gas) 15–19 (crystal)
$-CF_3$	Trigonal C Tetrahedral C	B_3 = 4–10 (cf. Ref.7) B_3 = 8–66 (cf. Ref.25)	4–7 (gas) 13–25 (gas) 11–17 (crystal, NMR)
$=PCl_3$	Trigonal N in phosphazo-compounds $Cl_3P=NR$	B_3 = 31–58	21–38 (crystal, NQR, NMR)
η^5-C_5H_5	Transition metals, Fe, Ni, Rh, Ru, Os	B_5 = 7–23	10–25 (crystal, NMR non-elastic neutron scattering)
η^5-C_5Me_4	Transition metals, Fe, Ru, Os	B_5 = 9–19	10–30 (crystal, NMR)

*From neutron diffraction data.

Multitemperature studies have played an important role in the investigation of the characteristics and features of the thermal vibrations of atoms in crystals. In the first place, such studies make

it possible to investigate the nature of the disorder,[7] revealing its static (associated with the coexistence in the same positions in the crystal of several different molecular orientations or conformations or with the multidomain nature of the specimen) or dynamic (associated with slow intramolecular movements characterised by a high amplitude) character. Such separation of the different types of ordering is naturally arbitrary because it can be determined only by the height of the barrier separating the crystal different orientations and conformers located in the same position in the crystal; furthermore, there is also a possibility of the presence in the crystal of both types of disorder.

Under the conditions of disordering of a static type, cooling of the crystals to specified temperatures should not lead to a consistent decrease in the temperature factors of the atoms in the disordered groups, which is natural since in the given instance large temperature parameters usually reflect only the presence in the crystal of molecules (or their fragments) with other orientations and conformations and not the occurrence of any atomic movement. On the other hand, in the study of systems with dynamic disorder one may expect a fairly sharp decrease in the temperature parameters of certain atoms in the structure when the temperature is reduced, since usually this type of disorder is associated with movements characterised by a fairly large amplitude and a low frequency, i.e. with the most readily "frozen out" types of vibrations. Certain examples of the use of low-temperature data in order to reduce disorder were examined above.

One may also note that the energy characteristics of the process considered can also be estimated from the analysis of the temperature variation of the populations of the individual sites in dynamically disordered structures. Thus a multitemperature study of 1,3,5-tribenzyl-1,3,5-triazacyclohexane (X) at 293, 268, 250, and 127 K [63] showed that the populations of the axial and equatorial positions of the N atoms change consistently with temperature, which corresponds to their inversion. The values of ΔH° and ΔS° for the inversion of the N atoms were calculated from diffraction data. Other examples of similar estimates were considered elsewhere.[11]

In a number of instances, interesting qualitative conclusions about the character of the conformational and sometimes chemical transformations of molecules in crystals can be reached only by analysing the shape of the thermal atomic ellipsoids. For example, in crystals containing molecules and complexes with saturated flexible five-membered rings, including metallocycles, one observes fairly frequently at room temperature a conformational disorder of the latter as a result of which two conformers coexist in the crystal (each has the half-chair form). The transition between them takes place via a pseudorotation mechanism.[64]

Numerous ethylenediamine complexes of metals constitutes a large group of such compounds. The individual orientations of the rings on electron density maps for such systems are usually not observed and disorder is as a rule manifested by the significant extension of the ellipsoids of the thermal vibrations of the C atoms of the ethylenediamine (en) ligands at right angles to the plane of the effectively flattened five-membered ring. The calculated effective amplitudes of the vibrations of the C atoms at right angles to the plane of the ring are anomalously large and amount to 0.3–0.4 Å; the C–C single bond then proves unrealistically short (~1.4 Å).[64] This disorder evidently has a dynamic nature, since, on cooling the crystals of these compounds, the metallocycles exhibit the half-chair conformation characteristic of them and the geometry of the ring becomes "normal". A similar change has been observed in a study of the complex $Cr(en)_3(SCN)_3.0.75H_2O$ in the temperature range 293–133 K,[65] the transition being fully reversible and continuous in character.

A similar disorder of the five-membered pyrrolidine ring has been observed in an X-ray diffraction study of sodium pyrrolidine-1-carbodithioate dihydrate $Na[S_2CN(CH_2)_4].2H_2O$ (XI) at 295, 150, and 27 K.[66] At 295 K, the ring is effectively flattened [the displacements of the C(4) and C(5) atoms from the plane of the S(1), C(1), and N atoms are 0.245(5) and −0.151(7) Å respectively], and thermal ellipsoids of the C(4) and C(5) atoms are greatly extended in the direction at right angles to the plane of the ring (Fig. 3), and, as a consequence of conformational disorder, the C(4)–C(5) single bond is unrealistically short: its length is 1.394(8) Å. At 150 K, the disorder is only partly frozen out [the displacements of the C(4) and C(5) atoms from the above plane are 0.269(6) and −0.259(6) Å respectively and the bond length C(4)–C(5) = 1.419(8) Å], in agreement with the height of the barrier to the pseudorotation of the pyrrolidine ring, which is commensurate with kT at 150 K. Complete ordering of the structure takes place at 27 K: the ring has the half-chair conformation, the displacements of the C(4) and C(5) atoms from the plane are 0.328(7) and −0.373(7) Å, and the bond length C(4)–C(5) = 1.511(10) Å, i.e. has the usual value for a $C(sp^3)–C(sp^3)$ single bond.

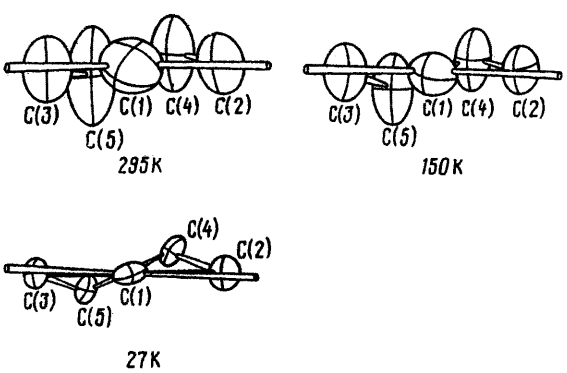


Figure 3. General form of the pyrrolidine ligand along the C(1)–N bond in the structure of sodium pyrrolidine-1-carbdithioate dihydrate (XI) at three temperatures (295, 150, and 27 K); the atoms are represented by thermal vibration probability ellipsoids.[66]

Analysis of the parameters of the atomic thermal displacements has also proved important in the study of many physical properties of crystals,[11] in particular in the study of the mechanisms of the structural and magnetic (spin) phase transitions, in the study of the properties of the liquid crystal state (the mesogen molecules are usually characterised by the presence of a hard central core and mobile side groups, which in the crystal execute much more vigorous vibrations than the central core of the molecule[67]), and in the study of biological macromolecules.[68,69]

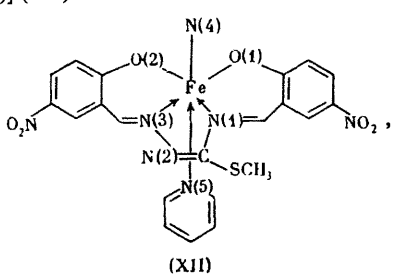
As an example, we shall consider the interesting type of disorder in a crystal, observed in the study of complexes containing Jahn–Teller ions (for example, Cu^{2+}) or compounds with spin transitions of the type "high-spin–low spin" in different octahedral iron complexes.

The degenerate electronic ground state ^2E_g of the Cu^{2+} ion for the ideal octahedral coordination of $[CuL_6]^{2+}$ (L is any ligand) is known to be unstable as a consequence of the Jahn–Teller effect, as a result of which the symmetry of the ion is reduced in order to remove the degeneracy.[70] The octahedral coordination of the ion is distorted, for example, to the tetragonal coordination, and these distortions actually lead to the disordering of the structure (because the tetragonal distortion axis can be any of the three directions in the octahedron). However, these distortions can be frequently small and they can therefore be detected only from the anomalous values of the temperature parameters of the $[CuL_6]$ fragment, which retains the average symmetry of the octahedron. Such anomalies are observed in the calculation of the differences Δ between the mean square "opposed" amplitudes of the atomic vibrations mentioned above. Table 2 presents data[42] for two isostructural compounds of the type $K_2PbM(NO_2)_6$ (M = Cu, Ni) characterised by the ideal octahedral symmetry of the anions $[M(NO_2)_6]^{4-}$ (all the M–N bonds are crystallographically equivalent).[42] The significant difference between the structures consists, however, in the fact that the Cu^{2+} complex is characterised by Jahn–Teller distortions and the existence of the ideal octahedron is therefore impossible for such an ion and the structure observed in the crystal is in essence disordered. As a consequence of this, the differences $\Delta_{M,N}$ for two the isostructural compounds differ almost by an order of magnitude: 0.0208(20) and 0.0022(10) Å^2. The magnitude of the Jahn–Teller distortion can be calculated from these differences (~0.14 Å).

Table 2. The mean square amplitudes U(Å^2) of the vibrations of the M (Cu, Ni) and N atoms in the direction of the bonds between them in the octahedral anions $[M(NO_2)_6]^{4-}$, the differences between them $\Delta_{M,N}$, and the distances R_{M-N}.[42]

Parameter	$[Cu(NO_2)_6]^{4-}$	$[Ni(NO_2)_6]^{4-}$
U_N	0.0380 (20)	0.0132 (9)
U_M	0.0172 (1)	0.0110 (1)
$\Delta_{M,N}$	0.0208 (20)	0.0022 (10)
R_{M-N}, Å	2.111 (4)	2.080 (2)

The study of an octahedral iron complex with a tetradentate asymmetric *S*-methylisothiosemicarbazide ligand L, i.e. [Fe(Py)(L).(NCS)] (XII)



(XII)

at 293 and 163 K showed[71] that, when the temperature is reduced, there is an appreciable change in the geometry of the coordination unit of the Fe atom, which can be caused by the transition of the metal atom to a low-spin state on cooling the specimen.

According to EPR and Mössbauer spectroscopic data, the Fe(3+) atom in compound (XII) is in a high-spin (S = 5/2) state at room temperature, while on cooling the compound a continuous phase transition to a low-spin (S = 1/2) state takes place, the transition being completed only at ~80 K. According to the results of Mössbauer analysis, the content of the high-spin form at 163 K (the temperature of the diffraction experiment) diminishes to ~20%, which alters significantly the geometry of the Fe octahedron: it contracts and the Fe–N bond involving the N(5) atom of the Py ligand is shortened by 0.105(4) Å; the decrease in the length of other Fe–N bonds is by 0.045–0.076(4) Å. At 163 K, the geometrical parameters of the FeN_4O_2 units are found to be close to those characteristic of the corresponding low-spin Fe(3+) complexes. However, the "failure" of the spin transition to reach completion at 163 K, i.e. the presence in the crystal of a residual disorder, is manifested distinctly by the anomalous values of the atomic thermal structural parameters at a low temperature. Thus the average value of the Hirshfeld differences Δ for the Fe–N and Fe–O bonds at 293 K (100% of the high-spin form) is 31 × 10^{-4} Å^2, whereas at 163 K (20% of the high-spin form and 80% of the low-spin form) this value increases by a factor of 3 to 91 × 10^{-4} Å^2. There is a corresponding sharp impairment at 163 K also of the formal parameters of the **LTS** model (R = 5.6% at 293 K and R = 18.6% at 163 K). (In the calculation of the **LTS** tensors, account was taken only of the atoms in the immediate environment of the metal.) The examples presented show that the parameters of the atomic thermal displacements can serve as reliable "indicators" of fine structural changes in crystals, in particular those associated with different phase transitions.

In conclusion of this part of the review, we may note that a real possibility of the extraction from precision X-ray data of quantitative information about the effective (one-particle) potentials of atoms in crystals has appeared recently.[72] The individual atomic temperature factors T(**q**) (**q** is the scattering vector) are Fourier transforms of the distribution function $P(R)$ (the probability density function) of the positions of the nuclei or electron density centroids (in neutron and X-ray diffraction respectively). In the classical high-temperature approximation, the function $P(R)$ can be written in the form

$$P(R) = \exp[-V(R)/kT] \Big/ \int \exp[-V(R)/kT]\, dR, \qquad (5)$$

where $V(R)$ is the potential energy of an atom vibrating in the effective field of its neighbours. Series expansion of $V(R)$ in powers of the displacement relative to the equilibrium position and the use of the quasi-harmonic approximation[72] makes it possible to recover the effective potential of the given atom in the crystal from the coefficients of the expansion. The expansion coefficients are usually refined by the least squares method. It is significant that the expansion need not necessarily be restricted to the harmonic members of the series; within the framework of this approach, it is also possible to take into account the anharmonicity of the atomic vibrations.

The first calculations of the effective atomic potentials were associated with the study of ionic conductivity[73] and the precision study of the electron distribution and anharmonicity of the atomic vibrations in the crystals of simple inorganic compounds.[74] Subsequently this approach was extended to studies on more complex compounds, in particular it was used to calculate the effective potentials of copper atoms in high-temperature

superconductors.[75] On the other hand, the concept of effective atomic potentials can prove useful also for the solution of various crystal-chemical problems. In particular, the force constants and the characteristic frequencies of the chemical bonds are related to the parameters of such potentials. The determination of the specific character of such a bond will probably make it possible to investigate at a higher level the different dynamic processes in crystals.

IV. Study of the distribution of electron density in crystals

The experimental determination of the distribution of electron density $\rho(r)$ in crystals and the discovery of the fine electronic structure of the chemical bond are some of the most important aspects of modern X-ray diffraction analysis.[6,17–19,76] Such studies make it possible to examine the principal ideas, which have become traditional, concerning the nature of the chemical bond in the language of the observed distribution $\rho(r)$. As already mentioned, the commonest method of investigation of the characteristics of the function $\rho(r)$ is the analysis of maps of the deformation electron density $\delta\rho(r)$ (DED), which has a simple significance. In particular, the form, position, and height of the $\delta\rho(r)$ maxima and/or minima relative to the atomic nuclei and lines connecting the chemically bound atoms make it possible to "visualise" the most important features of the electronic structure of molecules and crystals in the region of chemical bonds of different types.

The main principles of the interpretation of electron distribution maps have been described in a number of reviews[76–79] and monographs[17–19] and therefore there is no need to dwell on them in detail. We shall confine ourselves to characteristic examples of studies in recent years, referring mainly to the precision low-temperature study of the distribution of electron density in the crystals of simplest (usually low-melting) molecular compounds as well as certain more complex compounds of new types for which experimental electron distribution data were lacking until recently.

The importance of such investigations of the simplest compounds is determined primarily by the possiblity of carrying out for the purpose of such research of non-empirical quantum-chemical calculations of the electron distribution with a high level of accuracy, which makes it possible to compare theoretical and experimental data and to test the principal theoretical concepts developed for the description of the nature of the chemical bond. A critical comparison of such theoretical and experimental results has been made.[80,81] In addition, the fraction of valence electrons is frequently a maximum precisely in the crystals of the simplest compounds and the corresponding characteristic features of the DED maps, associated with the redistribution of the outer electrons of the atoms and the formation of chemical bonds, can therefore be recorded experimentally with a high accuracy and reliability.

We may note that the modern non-empirical calculations for molecules with a small number of electrons ($\sim$20–25) make it possible to evaluate the electron density in the internuclear space to within 0.05–0.10 e Å^{-3}. The possibilities of the diffraction experiment in the determination of the function $\rho(r)$ are somewhat greater — the accuracy of the determination of electron density in the region of the chemical bond reaches 0.02–0.04 e Å^{-3}.[18]

Apart from this, the X-ray diffraction method is applicable to the study of the electron distribution in complex polyatomic crystals and also in crystals containing the atoms of heavy elements ($Z < 70$). Non-empirical quantum-chemical calculations for such compounds, which require a high level of accuracy, are so far extremely laborious and few have been performed. Because of this, the precision X-ray diffraction method frequently proved to be the only available procedure whereby data can be obtained on the electron distribution in the study of complex compounds. The latter factor is extremely significant in the investigation of the distribution of electron density and of the characteristic features of the chemical bond in crystals of compounds of new types.

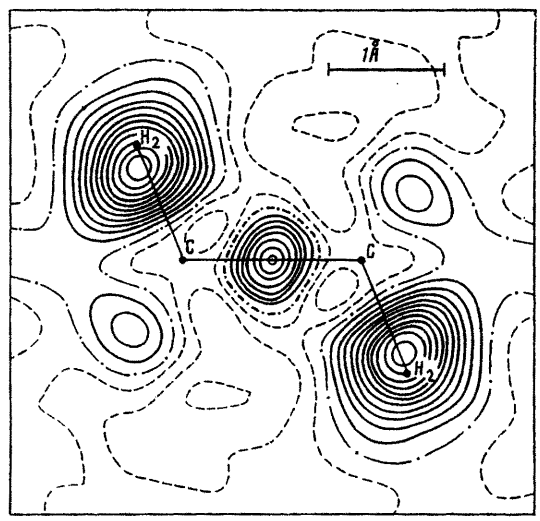


Figure 4. DED section through the transoid H–C–C–H fragment of the ethane molecule.[82] In this and subsequent figures, the continuous contours on the DED maps correspond to positive DED, the dashed lines correspond to negative DED, and dot and dash lines correspond to zero DED. The isolines are drawn at 0.05 e Å^{-3} intervals. [In the calculation of the DED for the ethane molecule, the electron density of the H atoms was not subtracted from the total density $\rho(r)$.]

Examination of the characteristic DED maps in the region of different chemical bonds can be usefully begun with the analysis of the results of the study of ethane, ethylene, and acetylene crystals — the simplest organic molecules containing single, double, and triple bonds between carbon atoms.[82] For the ethane molecule (data at 85 K), the DED section in the plane of the H–C–C–H transoid fragment is characterised by the presence of a distinct symmetrical maximum 0.35(4) e Å^{-3} high and located midway between the C atoms (Fig. 4). This result is consistent with the concept of the formation in ethane of a single covalent σ-bond (the C–C bond length in the crystal is 1.532 Å). In ethylene, the DED maximum on the C=C double bond with a length of 1.313 Å (data at 85 K) is characterised by a greater height (0.50 e Å^{-3}, Fig. 5*a*) and the presence of the π-component in the bond is manifested by a distinct extension of the DED maximum in the direction at right angles to the plane of the molecule and the bond line (Fig. 5*b*). The effectiveness of this π-interaction can probably be estimated from the degree of elongation of the ellipsoidal section (the ratio of the half-axes of the ellipse) in the plane at right angles to the

bond line. It is of interest to compare the result with the value of the so called bond "ellipticity" (ε) in ethylene $\varepsilon = \lambda_1/\lambda_2 - 1 = 0.74$, calculated quantum-chemically from electron density $\rho(r)$ data, where λ_1 and λ_2 are the eigenvalues of the $\rho(r)$ Hessian matrix in two mutually perpendicular directions at right angles to the bond line.[83]

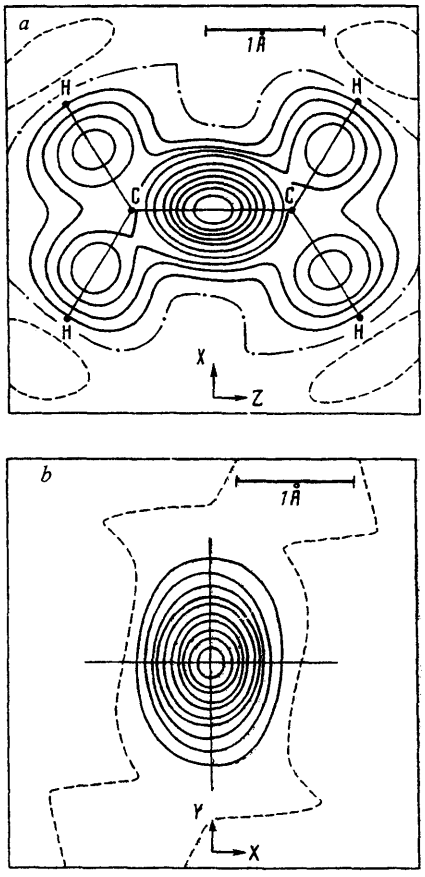


Figure 5. DED sections through the ethylene molecule in the plane of the latter (*a*) and in the plane perpendicular to the C—C bond and passing through its centre (*b*). The contours are drawn at 0.05 e Å^{-3} intervals.

The DED sections through the acetylene molecule (data at 141 K) are presented in Figs. 6*a* and 6*b*. The height of the DED maximum at the centre of the C≡C triple bond (1.182 Å) is 0.60 e Å^{-3} and the DED map actually coincides quantitatively with the results of the theoretical calculation for C_2H_2.[82] We emphasise that, since two π-bonds are formed in ethylene in mutually perpendicular directions, it follows that in the section normal to the C≡C bond line the characteristic ellipticity of the DED maximum is no longer observed (Fig. 6*b*).

The DED section in the plane of the C atoms of the cyclopropane molecule is illustrated in Fig. 7 (structural data[84] obtained at 94 K). It is characterised by the presence of distinct maxima located between the nuclei of the C atoms and displaced from the C—C bond line to the outer side of the triangle. The magnitude of the

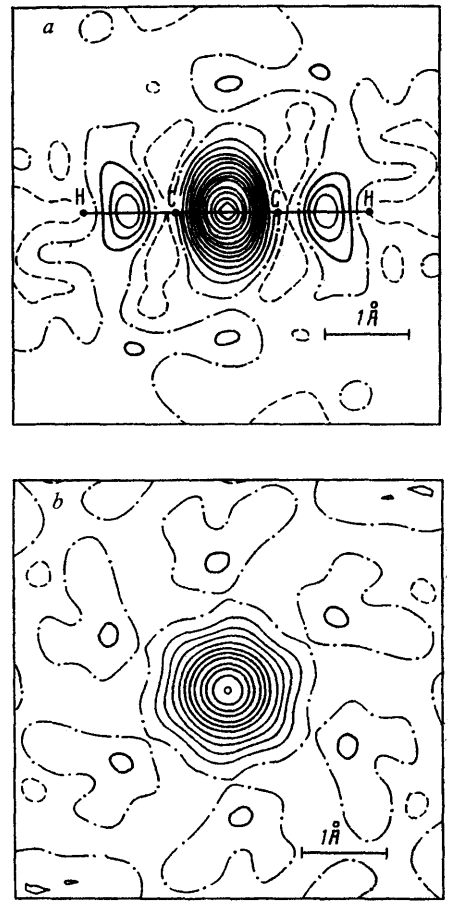


Figure 6. A DED map for the acetylene molecule (*a*) and the section in the plane perpendicular to the triple bond and passing through the centre of the molecule (*b*). The contours have been drawn at 0.05 e Å^{-3} intervals.

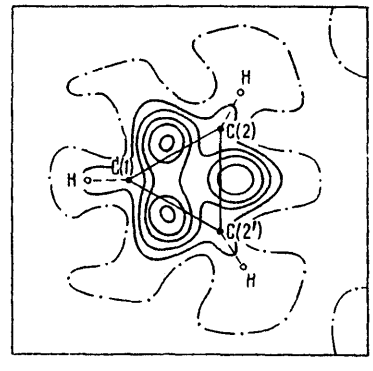


Figure 7. DED section through the plane of the C atoms of the cyclopropane molecule. The contours have been drawn at 0.05 e Å^{-3} intervals.

displacement is ~0.20 Å which constitutes clear confirmation of the ideas concerning "bent" bonds in strained small rings. A similar displacement of the DED maxima from the C–C bond line has been observed also in a series of other investigations of compounds with small rings or with strained three-membered frameworks. For example, in the tetra(t-butyl)tetrahedrane molecule, the DED maxima are displaced to the outer side of the tetrahedral molecular framework by 0.36 Å.[85] In perfluorotricyclooctane C_8F_{12} (XIII) (Fig. 8), investigated[86] at 163 K and containing condensed saturated four-membered rings, the DED maxima are displaced from the C–C bond line to a much lesser extent (~0.15 Å), which indicates a smaller bond strain in four-membered carbocycles compared with the three-membered rings.

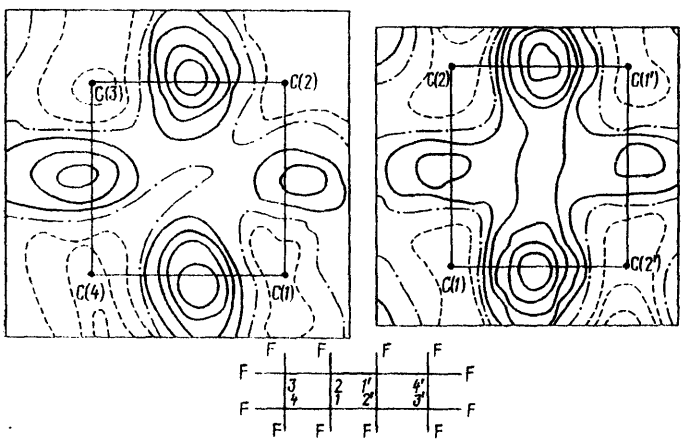


Figure 8. DED section in perfluorotricyclooctane (XIII) drawn through the planes of the four-membered rings of the molecule. The contours have been drawn at 0.1 e Å^{-3} intervals.

The examples considered above referred to molecules of organic compounds whose chemical bonds can be described within the framework of ideas concerning the formation of such compounds via the generation of localised two-centre bonds in them. In compounds where significantly **many-centre bonds with electron delocalisation** are formed according to existing ideas (for example in the molecules of borane or carbaboranes and in the cluster compounds of metals), the distribution of DED in the region of the bond is different. Figs. 9*a* and 9*b* present DED maps in sections drawn through the carbaborane nucleus (Fig. 9*a*) and the triangular B_3 and B_2C faces (Fig. 9*b*) of the icosahedron in the structure of 9-azido-*m*-carbaborane (XIV) [87] (the structural data were obtained at 163 K). In compound (XIV), the DED maxima are not distinctly localised on the B–B and B–C edges of the icosahedron or near the line connecting the atomic nuclei, as happens in the examples considered above. The excess (positive) DED is in fact distributed continuously in the region of the triangular faces but with a slight displacement of the DED on the B_2C face in the direction of the more electronegative C atom. The section through the centre of the icosahedron (Fig. 9*a*) shows that within the carbaborane framework the DED has a negative value (–0.16 e Å^{-3}) and the entire excess electron density is concentrated in a small spherical surface layer of the icosahedron and its distribution is virtually continuous. Thus, judging from the DED maps, the bonds in carbaboranes are formed as a result of the surface delocalisation of electron density, which agrees with the theoretical ideas put forward previously.[88]

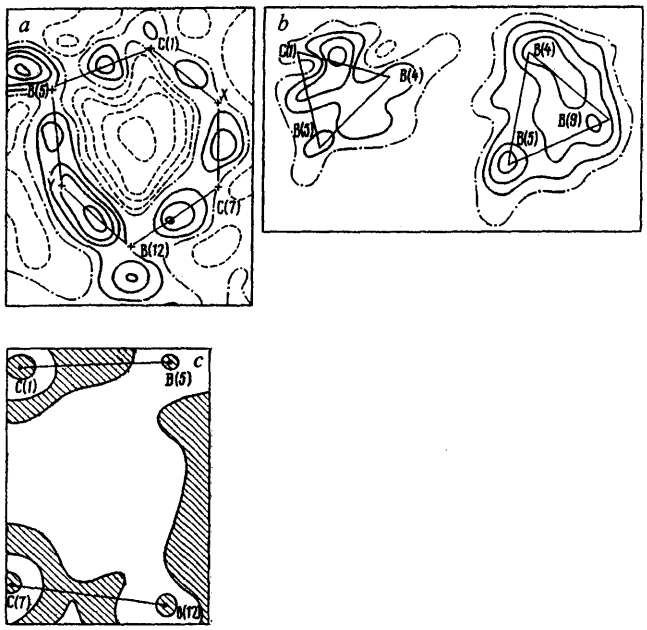


Figure 9. Distribution of electron density in 9-azido-*m*-carbaborane (XIV): *a*, DED section through the centre of the icosahedron passing through the C(1), B(5), C(7), and B(12) atoms and the centres of the B(2)–B(3) (*X*) and B(9)–B(10) (*Y*) bonds (the contours have been drawn at 0.04 e Å^{-3} intervals); *b*, DED section through the B_3 and B_2C triangular faces; *c*, $\nabla^2\rho(r)$ Laplacian section through the centre of the icosahedron passing through the C(1), B(5), C(7), and B(12) atoms (in the shaded regions, $\nabla^2\rho < 0$).

An additional confirmation of the results for compound (XIV) is provided by the calculation from the experimental data of maps of the electron density Laplacian $\nabla^2\rho(r)$ characterising the curvature of the function $\rho(r)$ in three mutually perpendicular directions. By definition, the Laplacian of the function $\rho(r)$ is the sum of the second partial derivatives:

$$\nabla^2\rho(r) = \frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2}, \qquad (6)$$

and, in conformity with the local formulation of the virial theorem for the energy of electrons $2E_{kin}(r) + E_{pot}(r) = {}^1/_4\nabla^2\rho(r)$,[89,90] the negative values of the function $\nabla^2\rho(r)$ in the molecular systems correspond to the parts of the space in which the local electron density is enhanced and in which the contribution of the potential energy stabilising the system predominates. Compared with the difference DED maps, the $\nabla^2\rho(r)$ maps have an important advantage: their construction does not necessitate the calculation of the electron density of the reference state

$$\rho^0(r) = \sum_{at} \rho^0_{at}$$

(of the premolecule), which is subtracted from $\rho(r)$ in the calculation of DED. For this reason, the $\nabla^2\rho(r)$ maps constitute an important and sometimes even a more informative complement of the DED maps used in the study of the electron distribution in crystals.[18] Fig. 9*c* presents the $\nabla^2\rho(r)$ map (the section was drawn through the carbaborane nucleus) of the molecule of compound (XIV), characterised by a wide range of positive values of the Laplacian within the carbaborane nucleus, i.e. the concentration of electron density is reduced within the nucleus, which is consistent with the form of the analogous DED map (cf. Fig. 9*a*). We also emphasise that in the vicinity of the C atoms there are in Fig. 9*c* regions $\nabla^2\rho(r) < 0$, i.e. regions of a local enhanced concentration of $\rho(r)$, which agrees with the greater electronegativity of these atoms compared with B atoms.

In the study of the electron distribution in compounds containing atoms with filled or more than half-filled valence shells (N, O, F, P, S, Cl, etc.), DED maxima are frequently observed near such atoms. They can be attributed to the sites where **the lone electron pairs (LEP) of these atoms are located.** Depending on the nature of the atom and the molecule and on the character of the crystal structure, the DED maxima can have significantly different heights, orientations relative to other bonds in the molecule, and degrees of diffuseness.

The characteristics of the manifestation of the lone electron pairs of the N and O atoms on the DED maps have been investigated frequently and in detail (see, for example, Breitenstein et al.[81]). These LEP are in fact always clearly seen on electron density maps and conclusions about the degree of hybridisation of the corresponding atoms can be reached from the character of their disposition.

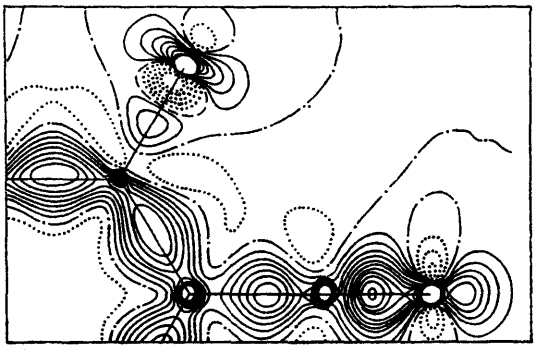


Figure 10. A static DED map in the plane of the $C_6F_4(CN)_2$ molecule (multipolar model). The contours have been drawn at 0.1 e Å^{-3} intervals.

We shall consider the characteristic features of the electron distribution in the region of LEP of halogen atoms. In the vicinity of the fluorine atoms, the LEP are as a rule manifested less distinctly, particularly in the construction of the DED maps by the traditional "$X-X$" method (see above), which is partly caused by their location near the F nuclei, where the error of the experimental determination of $\delta\rho(r)$ is large. Nevertheless, when more flexible, for example multiparameter multipolar models are used for the representation of DED, excess density maxima are observed near the F atoms and are disposed at right angles to the bond lines involving these atoms. As an example, one may quote data[91,92] obtained in the study of the electron distribution in a tetrafluoroterephthalodinitrile $C_6F_4(CN)_2$ (XV) crystal at 98 K [the error of the determination of the DED in compound (XV) in the region of chemical bonds is 0.02 e Å^{-3}; the DED maps were constructed using Hirshfeld's model[93] (Fig. 10)].

We may note that, in constructing the $\delta\rho(r)$ maps using the different multipolar models mentioned above, the electron density of the crystal is represented analytically by an expansion of $\rho(r)$, for example, in terms of angular harmonics or their combinations. The parameters of this expansion (the populations of the multipoles and the exponential multiplier in their radial components), as well as all the remaining positional and thermal parameters of the structure are refined by the least squares method. The first term in the expansion of the function $\rho(r)$ corresponds either to the electron density of the free atom $\rho^0(r)$ (Hirshfeld's deformation model[93]) or to the electron density $\rho_{int}(r)$ of the atomic core (the Stewart[94] or Hansen–Coppens[95] model).

More complex models for the analytical representation of $\rho(r)$ have also been proposed recently (see Porai-Koshits's review[18]) and it is significant that the analytical representation of the functions $\rho(r)$ and $\delta\rho(r)$ does in fact simplify the problem of the calculation of the properties of crystals which depend on these functions.[79] On the other hand, the multipolar representation of electron distribution data requires the refinement of a much greater number of independent parameters in least squares schemes. As a result of this, the use of low-temperature diffraction data in such studies on molecular crystals is sometimes essential, since only this makes it possible to secure a sufficient number of reflections (including large angle reflections) which are necessary for a significant refinement of additional multipolar parameters.

Characteristic examples are provided by data for $LiNO_3.3H_2O$ (at 295 and 120 K [96]) and imidazole (at 293 and 103 K [97]) crystals in which electron density was modelled with the aid of the Hirshfeld and Stewart multipoles respectively. In both cases, the authors pointed out the inadequate accuracy and amount of experimental data obtained at room temperature, which distorted the picture of the electron distribution.

Near the nuclei of covalently bound Cl atoms, the peaks corresponding to the LEP of the latter are shown clearly. In particular, in the study of the phosphorane $Cl_3P(CCl_3)_2$ at 153 K [56] the presence of effectively localised positive DED maxima, with a height of 0.2–0.3 e Å^{-3}, was established in the vicinity of the nuclei of Cl atoms. The maxima are at distances of 0.7–0.8 Å from these nuclei and are oriented in directions at right angles to the P–Cl and C–Cl bonds (Fig. 11).§ In terms of the character of their dispositions, these peaks should correspond to the LEP of Cl atoms having an appreciable p character. Furthermore, beyond the nuclei of the Cl atoms on the lines obtained by producing the P–Cl and C–Cl bonds, there are DED minima indicating the involvement of the p_σ orbitals of the Cl atoms in the formation of the corresponding bonds. We may also note an interesting feature of Fig. 11 associated with the presence on the axial "hypervalent" P–C bonds in this

§ The study of compound (VIII) at room temperature[57] indicated appreciable intramolecular vibrations of the CCl_3 groups, which hindered a reliable determination of the characteristic features of the DED maps.

compound of two intense DED maxima with heights of 0.35 and 0.40 e $Å^{-3}$. The presence of these maxima is consistent with the known fact that the axial disposition of electronegative substituents in pentacovalent phosphoranes is preferred.

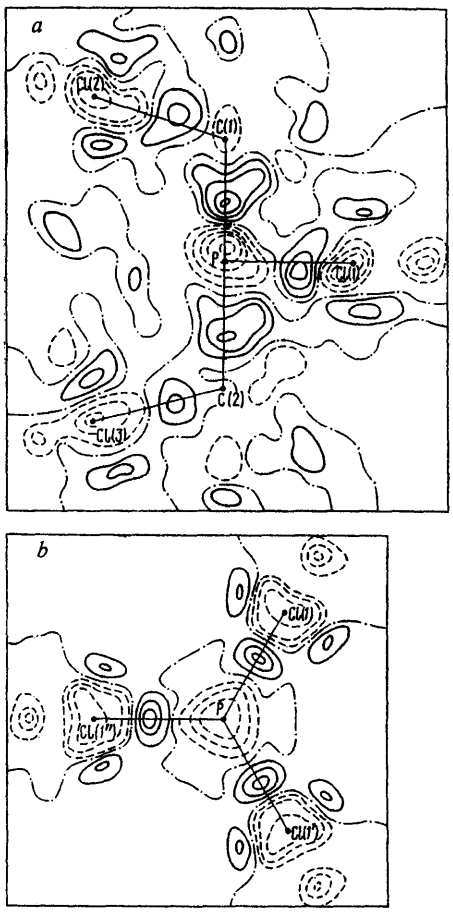


Figure 11. DED sections in the axial (*a*) and equatorial (*b*) planes of the phosphorane $Cl_3P(CCl_3)_2$ (VIII) molecule. The contours have been drawn at 0.1 e $Å^{-3}$ intervals.

An interesting example of the manifestation of the LEP of the Cl atoms on the DED maps has been observed in a study of the crystal of difluorochloronium tetrafluoroborate $ClF_2^+BF_4^-$ (data obtained[98] at 153 K). At room temperature, this readily hydrolysed compound consists of an equimolar mixture of gaseous ClF_3 and BF_3. On the DED map drawn in the bisector plane of the "angular" ClF_2^+ cation (with the angle F–Cl–F = 96.4°), there are in the vicinity of the Cl atom two maxima located at an angle of ~150° (Fig. 12), whose positions can be attributed to the localisation of the two LEP of the Cl atom. By building up the electron environment of the central atom to a distorted tetrahedron, these LP should occupy (according to Gillespie's ideas about the repulsion of electron pairs of the chemical bonds and the LP [99]) a larger solid angle in space than the electrons of the Cl–F bonds, which in fact increases the LP–Cl–LP angle in the ClF_2^+ cation compared with the tetrahedral value.

The data obtained agree with the results of a quantum-chemical calculation[100] of the positions of the regions of local higher concentration of electron density, i.e. with the calculation of the distribution of the Laplacian $\nabla^2\rho(r)$, according to which the angle between the minima in $\nabla^2\rho(r)$ in the region of the Cl–F bonds is 99° (the location of the valence electrons of the Cl–F bonds is consistent with this), while the angle between the $\nabla^2\rho(r)$ minima in the bisector plane of the cation is ~143° (the distance from the nucleus of the Cl atom to the centres of these minima is 0.604 Å).[100] Certain new data obtained in calculations of the $\nabla^2\rho(r)$ maps in order to locate the electron pairs of the halogen atoms have been discussed.[101]

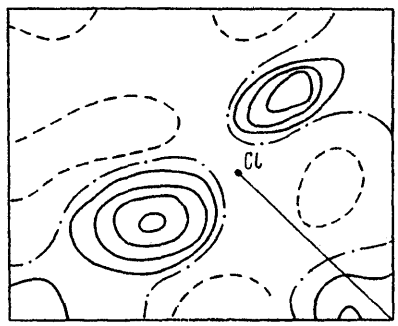
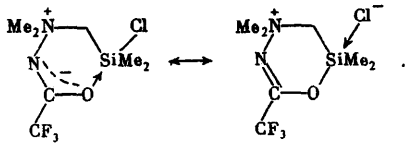


Figure 12. DED section in the structure of $ClF_2^+BF_4^-$ in the plane at right angles to the plane of the ClF_2^+ cation along the bisector of the F–Cl–F angle (the right-hand line). The contours have been drawn at 0.07 e $Å^{-3}$ intervals.

As a result of the improvement of the experimental diffraction method as well as the advances in the synthesis of compounds of fundamentally new types, which are frequently extremely unstable and have an unusual and complex structure, it has been possible in recent years to expand the research into the electron distribution in such compounds. In many cases, their great complexity precludes quantum-chemical calculation of the distribution of electron density in compounds of this kind, which makes the determination of experimental characteristics of their electronic structure of current interest. We shall consider examples of such studies in the series of **organoelement compounds.**

The study of the DED distribution in the trigonal-bipyramidal derivative of pentacoordinate silicon (XVI) was undertaken[102] as part of systematic structural investigations[103] of organosilicon compounds with additional intramolecular Si...O coordination in the "hypervalent" [O–Si–X] fragment. A precision study of compound (XVI) at 163 K showed that the Si atom is involved in trigonal-bipyramidal coordination with an axial disposition of the Cl and O atoms (the Cl–Si–O angle is 172° and the deviation of the Si atom from the equatorial plane of the three C atoms in the direction of the O atom is 0.076 Å). The Si–Cl = 2.434(1) Å bond in the molecule of compound (XVI) is very greatly lengthened, while the Si–O = 1.880(1) Å bond is close to the length of the covalent bond, although its length still exceeds somewhat the typical value for this bond. The C=O carbonyl bond in compound (XVI) has been lengthened to 1.285(2) Å, while the C=N = 1.289(1) Å bond actually corresponds to a double bond of the type $-N=C(sp^2)$.

The results suggest that the electronic structure of the molecule of compound (XVI) can be represented by the superposition of the "limiting" valence forms (A) and (B):



(XVI, A) (XVI, B)

The DED section in the axial plane of the molecule containing Cl, Si, O, and C(1) atoms shows (Fig. 13*a*) that one of the DED maxima near the O atom, whose height is 0.24 e Å^{-3} and which is usually attributed to the LP of this atom, is oriented precisely in the direction of the Si—O axial bond. On the other hand, an individual maximum was not observed on the Si—O bond, although its appearance might have been expected in the case of the formation of the usual covalent Si—O bond in compound (XVI). On the other Si—Cl bond, distinct positive DED peaks are visible only in the immediate vicinity of the nucleus of the Cl atom, while in the centre of the Si—Cl bond the DED is close to zero. In this respect, the DED map in the region of the bonds under consideration differs significantly from that found for similar but shorter (2.09—2.15 Å) Si—Cl bonds in the previously investigated trigonal-bipyramidal trichlorosilyltetrahydrophenanthroline derivative of pentacoordinate silicon.[104] The DED map in the region of the Si—Cl bond in this compound contains distinct maxima on the Si—Cl lines as well as maxima in the region of the LP of the Cl atoms located at right angles to the Si—Cl bond.

A similar picture of the DED distribution, characteristic of a covalently bound Cl atom, has been observed also in the region of the P—Cl and C—Cl bonds in the phosphorane (VIII) (Fig. 11). The data obtained for compound (XVI) evidently show that the Si—Cl bond in compound (XVI) can no longer be regarded as appreciably covalent and it is more likely that in this case a coordination interaction $Cl^- \rightarrow Si$ is observed [contribution by the form (B)]. This conclusion agrees with the increased length of the Si—Cl bond in compound (XVI) and also with the known fact[105] that, in nucleophilic substitution at a tetracoordinate silicon atom, the Cl atom is a "readily eliminated group" (as the Cl^- anion) from the axial position in the trigonal bipyramid of silicon.

The degree of electron delocalisation in the N(1)—C(1)—O amide group of compound (XVI), between the atoms of which there is a possibility of π-conjugation, can be estimated from the form of the DED sections passing at right angles to the C(1)—O and N(1)—C(1) bonds through their midpoints (Figs. 13*b* and 13*c*). A characteristic feature of these sections is the ellipsoidal form of the DED maxima, extended along the (*ab*) and (*cd*) lines perpendicular to the N(1)—C(1)—O plane illustrated by dashed lines in Figs. 13*b* and 13*c*. The form of the maxima constitutes clear confirmation (cf. the analogous section for ethylene—Fig. 5*b*) that the π-component contributes to the formation of the bonds under consideration and that in the case of the N(1)—C(1) bond this component is much more distinct than for the C(1)—O bond [contribution by the form (B)]. Thus the character of the electron distribution in the molecule of compound (XVI) clearly indicates the possibility of representing its electronic structure by a superposition of the forms (A) and (B) presented above. The data obtained from the analysis of the DED maps in compound (XVI) can be evidently used to model the character of the distribution of the electron density of the "transition state" of a S_N2 substitution reaction at the tetrahedral Si atom, which proceeds via the formation of intermediate trigonal-bipyramidal structures.

Another example is associated with the study of the electron distribution in a derivative of dicoordinate phosphorus in the phosphaalkene $(NMe_2)_2C{=}P{-}H$ (VIII) (structural data obtained[106] at 163 K). Phosphaalkenes—compounds with the $>C{=}P$-group are a comparatively new class of phosphorus derivatives and their simplest representatives, including compound (XVII), are as a rule low-melting and unstable. X-Ray diffraction study of a large group of phosphaalkenes demonstrated previously the high tendency of these compounds to conjugate the P=C double bond with the substituents at the P and C atoms,[107] which can lengthen appreciably the double bond to ~1.76 Å [in compound (XVII), the bond length P=C = 1.740(2) Å compared with the usual value of ~1.66 Å in the absence of conjugation]. In order to determine the qualitative characteristics of the electron distribution in phosphaalkenes, DED maps were constructed[106] in the region of the P=C and C—N bonds of the molecule of compound (XVII). Fig. 14*a* illustrates the DED section in the H—P=C plane [the displacement of the N(1, 2) from this plane is ±0.3 Å]. A characteristic feature of this map is the presence of the DED maximum on the P=C bond with a height of 0.39 e Å^{-3} and located approximately in the middle of the bond, and

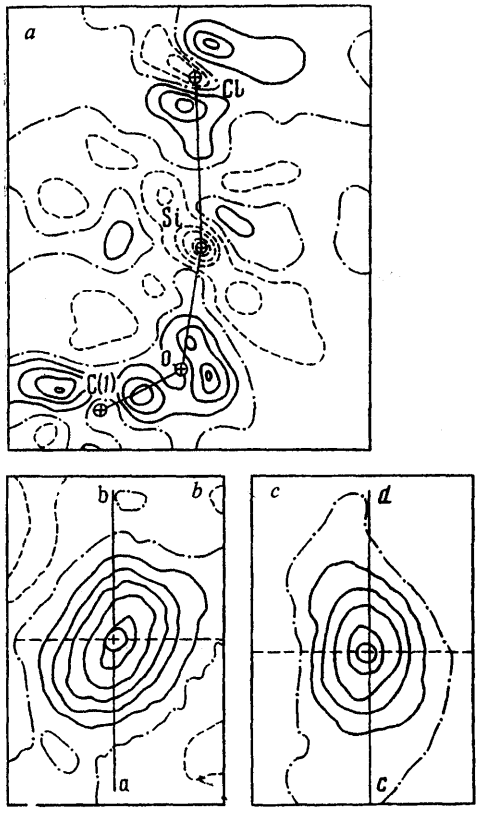


Figure 13. DED sections in the molecule of compound (XVI): *a*, in the axial plane through the Cl, Si, O and C(1) atoms (the contours have been drawn at 0.07 e Å^{-3} interval; *b*, and *c*, at right angles to the C(1)—O and C(1)—N(1) bonds and through the centres of the latter. The contours have been drawn at 0.05 (*b*) and 0.07 (*c*) e Å^{-3} intervals.

also of a maximum A (0.18 e Å^{-3}) located beyond the nucleus of the P atom at a distance of ~0.65 Å, lying in fact on the prolongation of the C=P bond line. In the plane of the π-bond (Fig. 14*b*), the DED maximum is characterised by an appreciable ellipticity, indicating a significant contribution of the π-component to the bond. A π-component of this kind can be seen also in the single C–N(1, 2) bonds, shortened to 1.348(4) and 1.391(4) Å, which is evidence for the occurrence of conjugation in the P=C=N chain.

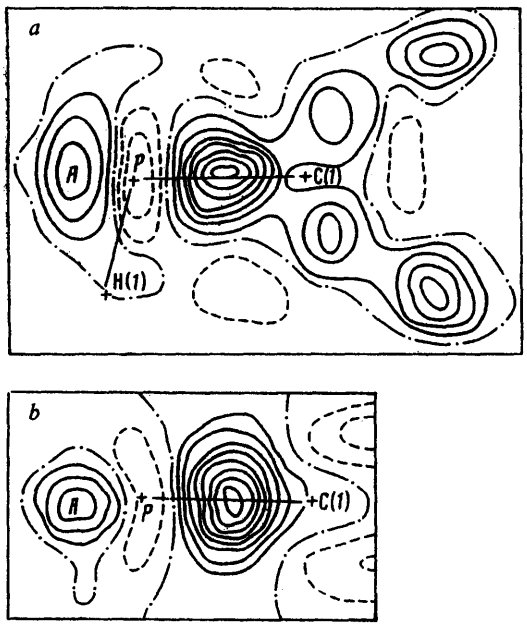


Figure 14. DED maps in the $(NMe_2)_2C=P-H$ (XVII) molecule: *a*, section in the plane of the H(1), P, and C(1) atoms (the contours have been drawn at 0.05 e Å^{-3} intervals); peak A—region of the LP of the P atom; *b*, section in the π-plane of the C=P bond (the contours have been drawn at 0.05 e Å^{-3} intervals).

The maximum A in the vicinity of the P atom is evidently associated with the location of the LP of this atom and from the character of its position one may conclude that the LP has appreciable *s* character. This conclusion agrees with the results of non-empirical quantum-chemical calculations for the simplest alkylidenephosphines.[106,108]

We may note that the significant *s* character of the LP of the P atom can explain the finding that, in the large series of structurally investigated phosphaalkenes (see the review of Chernega et al.[107]), the bond angle at the dicoordinate phosphorus atom is appreciably smaller than the value of 120° characteristic of the sp^2-hybridisation of this atom. Furthermore, the enhanced *s* character of the phosphorus LP in the compounds considered can be the reason why phosphaalkenes exhibit a lower reactivity than phosphines in oxidative addition reactions.[109]

Thus analysis of the DED maps made it possible in many instances to discover clearly the principal features of the electron distribution in the series of compounds of different types, agreeing with the traditional ideas about their electronic structure. In the language of electron distributions, particularly in terms of DED data, typical features of localised and delocalised (many-centre) bonds, strained (bent) bonds, π-bonds, hypervalent, coordinate, and dative bonds, etc. have been formulated and clear confirmation of many qualitative electron ideas used in chemistry has been obtained.

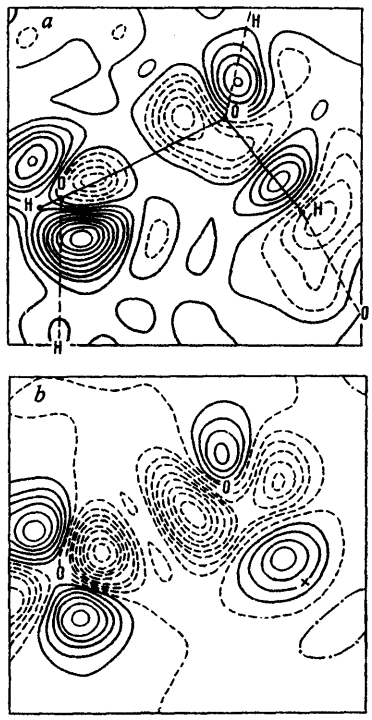


Figure 15. DED maps in the O–O–H plane of the hydrogen peroxide molecule: *a*, experimental data;[111] *b*, calculation.[113] The contours have been drawn at 0.1 e Å^{-3} intervals.

On the other hand, as DED data for different classes of compounds have accumulated, a series of **"strange" results** have appeared (see the review of Tsirel'son and Antipin[76]), which did not fit within the existing ideas about the electron distribution in the region of the chemical bond. In particular, the presence of only weak DED maxima or their complete absence from certain single covalent bonds between atoms whose valence shells are more than half-occupied proved to be difficult to understand. This result was observed in the study of the N–N bonds in a large group of hydrazine derivatives and on C–F, C–O, N–O, etc. bonds. For example, in the precision low-temperature study of 1,2,7,8-tetraaza-4,5,10,11-tetraoxatricyclo[6.4.1.1]tetradecane (III) (see above), it was found that the heights of the DED maxima on the bonds diminish systematically in the sequence C–N > C–O > N–N > O–O and in the region of the O–O bond the DED is actually negative.[110] In a series of other peroxide compounds, including hydrogen peroxide H_2O_2 (data obtained[111] at 100 K), the DED on the O–O bond is also negative (Fig. 15). These facts conflict with the traditional ideas about the formation of the covalent bond as a simple concentration of electron density in the space between nuclei, originating from early theoretical studies of the electron distribution

in the H_2 molecule; nevertheless the absence of significant DED maxima in the region of the bonds considered has been satisfactorily reproduced in quantum-chemical calculations.[81,112–114]

Detailed analysis of this problem carried out in a number of studies,[17–19,76,112–117] showed that the formation of a bond in the H_2 molecule has a number of specific features as a consequence of the absence from the molecule of steric restrictions on $\rho(r)$ imposed by the Pauli principle, and the H_2 molecule can therefore probably be regarded as a "classical" example in the study of the formation of a covalent chemical bond. The absence of DED peaks in the region of the bond considered is due to the fact that in such systems the rearrangement of electron clouds of the atom on formation of bonds proceeds in such a way that the outflow of electrons from the internuclear space as a consequence of the Pauli principle exceeds the effect associated with the increase in electron density in the same region as a result of the interference of the atomic electron clouds.[115] Since the DED maps illustrate the character of the redistribution of electron density relative to the "premolecule"[116] (an assembly of non-interacting atoms), the formation of the covalent bond proper is in many instances masked by other electronic effects (in particular, the transfer of part of the electron density from the internuclear space to the region of the LP), whose magnitude is greater the greater the degree of occupation of the valence shells of the atoms forming the chemical bond.

The foregoing permits the conclusion that the absence of positive DED in the region of the chemical bond is not essential evidence for the absence of a covalent bond and is frequently merely a result of the "oversubtraction" of the electron density, which is naturally not zero in the internuclear space of covalently linked atoms. Nevertheless, the information content of the DED maps is reduced in such cases.

We also emphasise that the presence of the DED maxima between atomic nuclei is likewise not always a sufficient condition for the formation of a covalent chemical bond.[118] In particular, the form of a theoretical DED map for the unstable Be_2 molecule does not differ qualitatively from the DED in stable diatomic molecules, for example in N_2: in both cases, $\delta\rho(r) > 0$ in the internuclear space.[119] Furthermore, even on formation of the simplest diatomic molecules, such as C_2, N_2, O_2, etc.,[84] the positive DED peaks are concentrated not only between the nuclei but also beyond them in the so called "non-bonding" regions, which diminishes, in conformity with Berlin's ideas,[120] the electrostatic forces linking the nuclei. Thus, in the analysis of DED maps and in their interpretation, it is essential to examine in detail all the positive and negative regions of such maps in the vicinity of the atomic nuclei, between which chemical bonds may (or may not) be formed.

It has been noted[118] that analysis of the changes in the electron distribution in the immediate vicinity of the atomic nuclei ($r < 0.4$ Å) is in many instances important for the understanding of the causes of the formation of a chemical bond. The electron density in these regions mainly determines the electrostatic forces acting on the nuclei, but this part of $\rho(r)$ is in fact fairly difficult to establish experimentally and theoretically with a high degree of accuracy. For example, in the multipolar analysis of the DED in the $C_6F_4(CN)_2$ (XV) molecule, it was found that the presence of a very weak $\delta\rho(r)$ maximum on the C–F bond (Fig. 10) cannot ensure the balance of electrostatic forces in the molecule required in accordance with the familiar Hellmann–Feynman theorem. In order to achieve this balance, one must take into account the polarisation of the inert electron clouds of the F atoms and, according to Hirshfeld,[92,121] such polarisation (deformation) of the atomic core can be detected experimentally when accurate X-ray and neutron diffraction data are used jointly and when the accuracy of the determination of the locations of the nuclei is to within $\sim 10^{-4}$ Å. Such an error may be attained only when diffraction data obtained at helium temperatures are used.

As a consequence of the difficulties in the interpretation of the DED maps listed above, other versions of the analysis of the experimental electron distribution data were developed in recent years, in particular methods for the calculation of maps of the **electron density Laplacian** $\nabla^2\rho(r)$ (see above) whose construction does not require the subtraction from $\rho(r)$ of the electron density of the "reference" state selected in a specific manner. Analysis of the Laplacian $\nabla^2\rho(r)$ is part of the study of the topological characteristics of the function $\rho(r)$ within the framework of Bader's theory,[88–90] which has now made possible the most rigorous definition of molecular structure, of an atom in a molecule, and of the chemical bond. A detailed discussion of the results of the analysis of the properties of the functions $\rho(r)$, $\delta\rho(r)$, and $\nabla^2\rho(r)$ within the framework of Bader's theory in relation to the study of the nature of chemical bonds of different types has been considered in a number of reviews.[18,76,83] Here we shall only emphasise that the joint analysis of the functions $\delta\rho(r)$ and $\nabla^2\rho(r)$ derived from the results of a precision diffraction experiment made it possible to deepen the existing ideas about the chemical bond.

In conclusion of the review, we shall consider briefly the possibility of using precision diffraction data, including DED maps, for the interpretation of the characteristic features of **the chemical reactivity of compounds.** We may note that so far there are few examples of such studies, although problems of the relationship between the reactivity of molecules (for example, their capacity for protonation) and their quantum-chemically calculated electrostatic properties, in particular their molecular electrostatic potential (MEP), have been considered in fair detail in the literature.[122] The MEP maps, calculated by quantum-chemical methods, have a simple physical significance, namely the MEP minima must correspond to protonation centres in the compound considered.

The similarities and differences between the corresponding MEP and DED maps for relatively simple molecular compounds have been investigated in a number of studies[122–125] and it has been shown that in many cases such maps are topologically similar. Thus, by formulating, using the procedure of Weber et al.,[125] the electrostatic potential $V(r)$ at a point r for the molecular system, characterised by the electron density distribution function $\rho(r)$, as the sum of the electronic and nuclear components, we have

$$V(r) = -\int \frac{\rho(r')}{|r-r'|}\,dr' + \sum_A \frac{Z_A}{|R_A - r|}, \qquad (7)$$

where Z_A is the nuclear charge of the atom A with the coordinates R_A (summation with respect to all the atoms in the molecule). After introducing the electron density of the premolecule

$$\rho^\circ(r') = \sum_A \rho_A^\circ(r'),$$

the expression for $V(r)$ can be put in the equivalent form

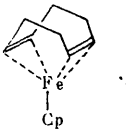
$$V(r) = -\int \frac{\rho(r') - \sum_A \rho_A^\circ(r')}{|r-r'|}\,dr' + \sum_A \left(\int \frac{-\rho_A^\circ(r')}{|r-r'|}\,dr' + \frac{Z_A}{|R_A - r'|} \right). \qquad (8)$$

The expression in round brackets in the last sum is the atomic electrostatic potential $V_A(r)$ and Eqn. (8) can therefore be written thus:

$$V(r) = -\int \frac{\delta\rho(r')}{|r-r'|}\,dr' + \sum_A v_A(r). \qquad (9)$$

It has been shown by Politzer[126] that in the vicinity of an atom the quantity $V_A(r)$ is positive and the sign of the potential is therefore determined by the sign of $\delta\rho(r)$ (the DED function) and by the integral in Eqn. (9). It follows from Eqn. (9) that the negative regions of MEP (the possible centres for protonation or electrophilic attack) in molecules can be mutually related to regions in which there are electron density maxima on the corresponding DED maps.

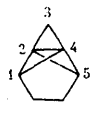
We shall consider certain examples confirming the foregoing. Thus, a precision study of the DED (data obtained[78] at 100 K) of the 17-electron π-cyclopentadienyl-η^4-cycloocta-1,5-dienyl iron complex (XVIII) and its adduct with Li(TMEDA) (TMEDA = tetramethylethylenediamine) established that the Li atom in the adduct is located in the direction of the sterically most accessible (least shielded) of the group of DED maxima near the Fe atom of the initial complex (XVIII), in which these maxima, associated with the populated 3*d* orbitals of the metal atom, are arranged octahedrally.



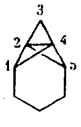
(XVIII)

The results may indicate a significantly electrostatic character for the Fe...Li interaction and may illustrate the possible direction of electrophilic attack on the metal atom. Another similar example is a study[127] of the DED in the "cubane-like" tetrahedral chromium cluster $(\eta^5\text{-}C_5H_4Me)_4Cr_4(\mu_3\text{-}S)_4$ (XIX). On the DED map of this compound, DED maxima were observed on the outer side of the SCr_3 tetrahedra beyond the S atom. They were interpreted as corresponding to the LP of these atoms. As a result of precisely this feature of the electron distribution, the μ_3-ligand of the cluster retains the capacity for weak additional "external" S...Cu coordination in complex (XIX) with $CuBr_2$.

An interesting result has been obtained recently in a study of two highly reactive [1.1.1]propellane derivatives (XX) and (XXI) (data obtained[128] at 81 K):



(XX)



(XXI)

The lengths of the C(2)–C(4) bridge bonds between the "inverted" carbon atoms in these molecules are 1.587 and 1.585 Å, the DED in the region of the C(2)–C(4) bonds being negative and close to zero (Fig. 16). On the other hand, on the outer side of the bridge bonds near the C(2) and C(4) atoms there are DED maxima 0.10–0.15 e Å^{-3} high. Indeed, according to Wiberg et al.,[129] the ease of the protonation of [1.1.1]propellane is responsible for the marked tendency of this compound to undergo acetolysis. The presence of the above non-bonding electron density maxima at the inverted carbon atoms in propellane derivatives has been confirmed[130] by calculations of maps of the electron density Laplacian for such compounds.

A new approach to the theoretical study of the nature of chemical reactivity, based on the analysis of the characteristic features of the electron distribution $\rho(r)$ and the characteristics associated with $\rho(r)$, in the first place the Laplacian $\nabla^2\rho(r)$, was proposed by Bader et al.[100] This approach proved to be closely related to the familiar method of Fukui's "frontier orbitals".[132] It was shown that the regions where the HOMO and LUMO frontier molecular orbitals are located in space correspond in the case of many compounds to regions of local concentration or rarefaction of electron density and the positions of the latter can be determined from the analysis of $\nabla^2\rho(r)$. In particular, analysis of the characteristic features of the function $\rho(r)$ for a series of carbonyl compounds indicates the presence in the valence environment of the C atom of the so called "critical" saddle points in the distribution of $\rho(r)$, where $\nabla(\nabla^2\rho) = 0$; they are distributed near the C atoms at an angle of ~110° relative to the C=O bond line above and below the plane of the carbonyl group.[100] Nucleophilic attack on the carbon atom actually takes place at this angle, which has been confirmed by the results of structural studies.[42] In addition to the foregoing, we may note also the results of studies[133,134] in which analysis of the quantum-chemically calculated $\nabla^2\rho(r)$ maps led to a conclusion about the mechanism of the opening of the three-membered ring in the protonated dimethyloxiran $(CH_3)_2\overline{CCH_2OH}^+$ on treatment with nucleophiles.

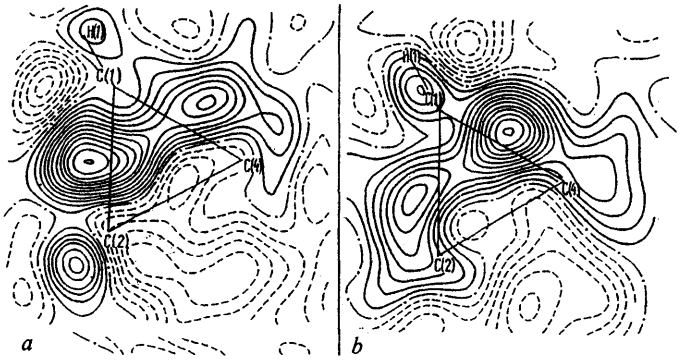


Figure 16. DED sections in the [1.1.1]propellane derivatives (XX) (*a*) and (XXI) (*b*) drawn through the C(1)–C(2)–C(4) atoms of the three-membered rings. The contours have been drawn at 0.025 e Å^{-3} intervals.

The above examples show that, in the field of study of the physicochemical properties of various compounds, the precision X-ray diffraction method can yield new interesting information about the character and features of the distribution of electron density in molecules. However, only the first steps have been taken in this direction. The expansion of the range of compounds investigated and also further improvement of the experimental accuracy of the method and of its computational techniques should evidently lead to the appearance of new and important results in the immediate future.

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Characteristic features of the crystal chemistry of lanthanide molybdates and tungstates

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ABSTRACT. The review gives a systematic account and analyses the characteristic features of the chemical composition, crystal structures, and properties of lanthanide molybdates and tungstates. The structure forming role of molybdenum(VI), tungsten(VI), and the lanthanides(III) in oxide compounds is discussed within the framework of the bond valence force model and ideas concerning non-bonding intercationic interactions. The theoretical conclusions as regards the correspondence between the compositions, structures, and properties of the compounds are compared with experimental data.

Contents

I. Introduction 627
II. The structure forming role of molybdenum (VI), tungsten(VI), and the lanthanides(III) in oxide compounds 627
III. Chemical compositions of the compounds formed in the $Ln_2O_3-EO_3$ systems 634
IV. Structure and properties 636
V. Conclusion 638

I. Introduction

The $Ln_2O_3-EO_3$ systems, where Ln = La–Lu and Y while E = Mo and W, are the few pseudobinary systems in which the existence of a large number of intermediate compounds has been reliably established. Many molybdates and tungstates exhibit a complex polymorphism. Many of them are distinguished by qualities of practical value. Refractory, luminescent, magnetic, piezoelectric and ferroelectric, and ferroelastic properties are frequently successfully combined in a single material.[1–3] The systematic study of phase formation in the $Ln_2O_3-EO_3$ systems, initiated in the 1960s, was initially designed for applied purposes and was characterised by a combined application of methods of physicochemical analysis and the determination of physical properties.

As a result of vigorous research, the phase relations in the above systems have been elucidated schematically in broad outline but this scheme is not final owing to the contradictory interpretation of individual details of these systems by different workers. There are objective reasons for this: the experimental difficulties in high-temperature studies, the multiplicity of phase transformations in the compounds formed, the characteristic features of the kinetics of the solid-phase reactions, and the difficulty and frequently the impossibility of isolating many phases as single crystals. For example, the $La_2O_3-WO_3$ system and the compounds formed in it have been frequently studied,[4–27] but there is nevertheless no complete certainty[25–27] about the reliability of the phase diagram (Fig. 1 [23]) constructed from the results of high-temperature (up to 2000 °C) X-ray diffraction analysis and differential thermal analysis (DTA) in view of the ultrafast quenching used ($\sim 10^5$ K s^{-1} [19]). Not only the width of the phase regions but also the very fact of the formation of certain chemical compounds and their composition have been questioned. In all probability these and similar controversial questions will soon be resolved by virtue of the progressive development of methods for structural chemical analysis,[28] a number of examples of which already exist.[29–34]

Literature data are now available for more than 40 structural types of lanthanide molybdates and tungstates, 24 of which have been elucidated (Table 1). Lanthanide molybdates and tungstates resemble structurally both complex transition metal oxides and typical salt-like compounds of the type of sulphates. Their crystal structures have the same characteristic features as classical inorganic compounds. This factor is particularly valuable because it facilitates the crystal-chemical analysis of the relationship between chemical composition, structure, and properties of the test systems.

II. The structure forming role of molybdenum(VI), tungsten(VI), and the lanthanides(III) in oxide compounds

In recent years a trend has arisen in descriptive inorganic crystal chemistry towards a shift of priorities from the topological and geometrical analysis of structures to the solution of problems involving bonding and non-bonding interatomic interactions.[78–80] This has been promoted to a considerable extent by the high accuracy of the determination of the positions of atoms achieved in the structural analysis of single crystals, the high speed of such analysis, and hence the creation of an extensive and rapidly increasing stock of experimental data. All these factors create favourable conditions for far-reaching theoretical generalisations whose development is passing through the stage involving the development of empirical models describing observed phenomena with a high degree of statistical reliability.

1. The bond valence force model

In analysing the characteristic features of the structures of crystals of inorganic compounds, which possess predominantly chemical bonds of the ionic type, the concepts of the ionic radius, the coordination polyhedron, and close packing are traditionally used.[81] The characteristic features of the structures of such compounds were first treated systematically by Pauling and were formulated[82] in the form of five principles (or rules) a list of which, frequently described

rather freely, can be found in the scientific literature.[81] Since the 1970s, investigators returned to Pauling's concept because a broader significance of Pauling's postulates became apparent than the author himself imagined initially.[82] In the 1980s, a quantum-mechanical justification of Pauling's rule was discovered. This applies to the greatest extent to the so called "second rule"—the electrostatic valence principle.[83]

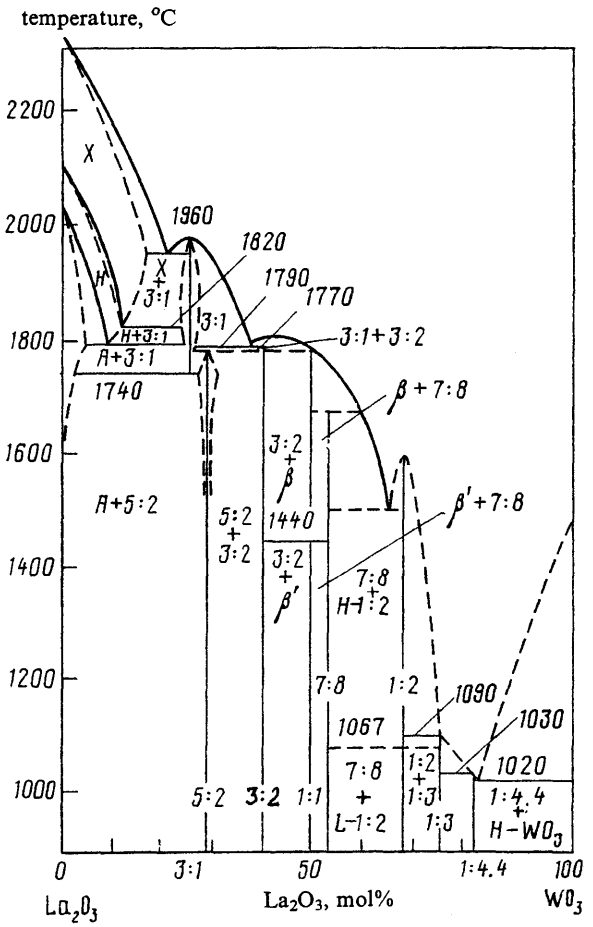


Figure 1. Phase diagram for the La_2O_3—WO_3 system.

In formulating this rule Pauling[82] introduced the concept of "bond strength". In the Soviet literature, the term "valentnoe usilie svyazi" ("bond valence force") became firmly established but the terms "sila", "prochnost'", "valentnost'" svyazi (bond "force", "strength", and "valence") are also used. Pauling's bond strength is defined as the ratio of the formal valence of the cation (V_M) to its coordination number (CN_M):

$$S = V_M/CN_M. \quad (1)$$

The original formulation of the rule was as follows:[82] in a stable coordination structure, the electrical charge of each anion tends to compensate for the force of the electrostatic valence bonds originating from the cations at the centres of the polyhedra whose vertices are occupied by the anion. Zachariasen[84] gives a somewhat different formulation: the sum of the valence forces of the bonds with the cations (pX), converging on the anion, neutralises the charge of the latter (V_X):

$$p\mathrm{X} = \sum_j S_j \simeq V_\mathrm{X}. \quad (2)$$

In such description, the rule has an "electrostatic" content but subsequently it began to be extended also to partially ionic covalent bonds.[85]

In the case of the simplest inorganic structures, in which there are anions of only one crystallographic kind, this rule is known to hold *a priori* by virtue of the requirement for the electrical neutrality of the crystal structure, but if the system is more complex, the exact or approximate fulfilment of this requirement cannot be regarded as self-evident. With increase in the number of elucidated structures, large groups of systems, for example heteropoly-compounds and isopoly-compounds,[86,87] were discovered, in which this rule breaks down. Thus, in the case of $[HN_3P_3(NMe_2)_6]_2Mo_6O_{19}$,[88] the six MoO_6 octahedra have a common oxygen vertex, i.e. when Eqns. (1) and (2) are formally applied one can arrive at the paradoxical conclusion that the nominally divalent oxygen atom is "neutralised" by six (pO = 6 × 6/6) valence units (v.u.) arising from the bonds with Mo(VI).

The objections against the rule became so strong that important advantages of the model such as the possibility of assigning with its aid the oxygen atoms in minerals to O^{2-}, OH^-, and H_2O were consigned to oblivion. It was not until the end of the 1960s that attention was drawn to the relation between the bond length R(M—O) and the sum of the valence forces [bond strengths] (pO) defined by Eqn. (1): the higher the value of pO, the greater the M—O bond length.[88] In the 1970s, this conclusion was supported by a multiplicity of data referring to reliably elucidated structures of oxide compounds of different classes. In 1970, Bauer[89] proposed the "extended electrostatic valence rule" based on the statistical analysis of 14 kinds of coordination polyhedra ranging from BO_3 to KO_8, according to which the following relation holds with a high degree of reliability (the correlation coefficients are close to 1.0):

$$R(\mathrm{M—O}) = a + b \cdot p\mathrm{O}, \quad (3)$$

where a and b are empirical coefficients having individual values for each kind of polyhedra. The empirical expression (3) for cations whose formal valence is less than 3 can be regarded as qualitative because in this case there is an appreciable scattering of data. Nevertheless, for cations with a higher valence, Eqn. (3) has great predictive power. Problems concerning the rapid testing of the reliability of structural determinations, the establishment of the presence of hydrogen bonds, and even the prediction of interatomic distances and bond angles in PO_4 tetrahedra on the basis of a qualitative scheme specifying the way in which these polyhedra are surrounded by other cations in concrete structures were solved.[90]

The numerical coefficients of Eqn. (3) have been analysed.[91] By means of elementary transformations, the authors[91] found that

$$(R_i - \bar{R})/\bar{R} = b(p\mathrm{O}_i - 2), \quad (4)$$

where R_i is the individual M—O_i bond length, R the average bond length in the polyhedron, and b an empirical constant. Eqn. (4) means that the change in the length of an individual bond in the polyhedron relative to the average value for the polyhedron is proportional to the difference between the valence of the oxygen

Table 1. Structural types of compounds in the $Ln_2O_3-EO_3$ systems.

Chemical composition $nLn_2O_3:mEO_3$	Formula	Structural type*	Representatives E=Mo	Representatives E=W	Crystal system space group	Representatives Ln	Representatives E	Unit cell parameters a, Å	b, Å	c, Å	angles, deg	Remarks	Refs.
3:1	Ln_6EO_{12}	Pseudofluorite	La—Er, Y	La—Lu, Y	Cubic, *F*	La	W	11.177					[9, 13, 18, 35]
	Lu_6UO_{12} *	Ho—Lu, Y	Tb—Lu, Y	$R\bar{3}$	Lu	W	9.617		9.151			[13, 36—38]
	»	La(?)Nd(?)		$R\bar{3}$ (?)	La	Mo	10.54		9.878			[37, 38]
5:2	$Ln_{10}E_2O_{21}$	$Y_{10}W_2O_{21}$ *	Nd(?)	Nd—Er, Y	*Pbcn*	Er	W	15.82	10.48	10.54			[29, 32]
	Pyrochlore	La	La	*Fm3m*	La	W	11.167					[18, 37]
«9:4»**	$Ln_{18}E_4O_{39}$	Pseudofluorite	Nd—Tm, Y		Trigonal, *R*	Nd	Mo	10.27		9.69		Subcell	[39]
«2:1»**	Ln_4EO_9	»	La, Nd		?							Not determined	[39, 40]
«7:4»**	$Ln_{14}E_4O_{33}$	»		Nd—Dy	Pseudo-*R*3	Dy	W	3.699		9.465		Subcell	[13]
		»		Ho, Y	»	Y	W	3.684		9.401		»	[13]
		»		Er—Lu	Trigonal	Er	W	7.375		9.308		»	[13]
3:2	$Ln_6E_2O_{15}$	$La_6W_2O_{15}$		La—Nd	*Cmma*	La	W	25.26	17.82	11.93			[21]
		$La_6Mo_2O_{15}$	La	La	Orthorhombic	La	Mo	12.60	5.930	8.888			[37]
1:1	Ln_2EO_6	I — Ln_2WO_6		La, Ce	Orthorhombic	La	W	7.52	12.80	10.35			[27, 41]
		II — Ln_2WO_6 *	La—Lu, Y	Ce—Ho, Y	*C*2/*c*	Nd	W	16.63	11.38	5.52	β=107.6		[42—46]
		III — Ln_2WO_6 *		Dy—Lu, Y	*P*2/*c*	Y	W	7.59	5.33	11.35	β=104.4		[45, 47, 48]
		IV — Ln_2WO_6 *		La—Ho, Y	$P\bar{4}2_1m$	Y	W	5.26		8.44			[14, 41]
		V — Ln_2WO_6 *		Pr—Er, Y	$P2_12_12_1$	Y	W	5.21	9.02	9.91			[33, 48]
		VI — Ln_2WO_6 *		Y	$P2_12_12_1$	Y	W	8.59	20.84	5.23			[49, 50]
		VII — Ln_2WO_6 *		Er—Yb	*Pbca*	Er	W	15.77	10.52	5.52			[34]
		X — Ln_2MoO_6 *	La—Sm		$I4_1/acd$	Nd	Mo	5.66		31.6			[43, 51]
		X′ — Ln_2MoO_6 *	La—Sm		$I\bar{4}cd$	La	Mo	5.80		32.0			[51]
		XI — Ln_2MoO_6	La—Nd		$Pca2_1$ (?)	Pr	Mo	5.54	16.60	5.55			[52]
«7:8»**	$Ln_{14}E_8O_{45}$	Group of polytypes		La	Hexagonal	La	W	9.05		33.25		For $n=6$	[22, 24]
«6:7»**	$Ln_{12}E_7O_{39}$	?	Nd, Pr		?							Not determined	[53]
		?		Nd	?							»	[54]
«4:5»**	$Ln_8E_5O_{27}$	?		Pr	?							»	[55]
2:3	$Ln_4E_3O_{15}$	$Nd_4W_3O_{15}$ *		La—Nd	$P4_2/nmc$	Nd	W	9.92		12.50			[11, 56]
1:2	$Ln_2E_2O_9$	I — $La_2Mo_2O_9$	La, Pr	La—Nd	Cubic	Nd	W	7.00	9.83		β=107.5*		[13, 40, 57]
		II — $Pr_2W_2O_9$ *		Ce—Gd	$P2_1/c$	Nd	W	7.64		9.22			[13, 58]
		III — $La_2W_2O_9$		La	?							Not determined	[22, 26]
1:3	$Ln_2(EO_4)_3$	A, scheelite*	La, Ce		$I4_1/a$	La	Mo	5.365		11.94			[2, 59]
		*A*1 — $La_2(MoO_4)_3$ *	La—Nd		*C*2/*c*	La	Mo	17.01	11.95	16.09	β=108.4		[2, 60]
		*A*2 — $Nd_2(MoO_4)_3$ *	Nd		*C*2	Nd	Mo	27.02	11.71	11.85	β=105.3		[59]
		*A*3 — $Eu_2(WO_4)_3$ *		La—Ho	*C*2/*c*	Eu	W	7.68	11.46	11.43	β=109.6		[61, 62]
		*A*4 — $Sm_2(MoO_4)_3$	Sm—Dy		*Cc* (?)	Eu	Mo	7.55	11.46	11.50	β=109.1		[2]
		*A*5 — $La_2(WO_4)_3$		La	?	La	W					Not determined	[14]
		L — $Gd_2(MoO_4)_3$ *	Pr—Ho		$P\bar{4}2_1m$	Gd	Mo	7.35		10.70			[2, 63—65]
		*L*1 — $Gd_2(MoO_4)_3$ *	Pr—Ho		*Pba*2	Gd	Mo	10.39	10.42	10.70			[61, 65—67]
		*L*2 — $Gd_2(MoO_4)_3$	Gd		Tetragonal	Gd	Mo	14.69		10.70			[68]
		*L*3 — $Gd_2(MoO_4)_3$	Gd		$Pna2_1$	Gd	Mo	10.39	10.42	21.40			[69]
		J — $Tb_2(MoO_4)_4$	Tb		Cubic	Tb	Mo	10.44					[61]
		G — $Dy_2(MoO_4)_3$	Dy		Cubic	Dy	Mo	6.69					[2]
		C — $Sc_2(WO_4)_3$ *	Dy—Lu, Y	Gd—Lu, Y	*Pbcn*	Lu	Mo	13.69	9.83	9.93			[2, 70, 71]
		*C*1 — $Tm_2(MoO_4)_3$	Dy—Tm		Orthorhombic	Tm	Mo	13.45	9.78	19.8	α=103,		[2]
3:10	$Ln_6E_{10}O_{39}$	$Ce_6(MoO_4)_8(Mo_2O_7)$ *	Ce		$P\bar{1}$	Ce	Mo	10.15	18.76	9.57	β=78, γ=108		[30]
1:4	$Ln_2E_4O_{15}$	$La_2Mo_4O_{15}$	La		?							Not determined	[57, 72, 73]
		$Ce_2Mo_4O_{15}$ *	Ce—Sm		$P\bar{1}$	Pr	Mo	7.39	7.51	11.82	α=89, β=97, γ=95		[31, 74]
		$Sm_2Mo_4O_{15}$	Pr—Tb		?							Not determined	[57, 73]
		$Ho_2Mo_4O_{15}$ *	Gd—Lu, Y		P2/*c*	Ho	Mo	6.82	9.59	10.53	β=105.6		[73, 75]
5:22	$Ln_{10}E_{22}O_{81}$	$Sm_{10}W_{22}O_{81}$ *		La—Sm	*Pnma*	Sm	W	35.34	21.82	3.839			[20, 76]
1:6	$Ln_2E_6O_{21}$	$Nd_2(Mo_3O_7)_3$*	La—Td		P4/*nnc*	Nd	Mo	8.97		26.45			[76, 77]

* The asterisk denotes structures which have been elucidated. ** The chemical composition has not been confirmed.

atom calculated by Eqns. (1) and (2) and its formal value, which is 2. Each type of polyhedra can then be characterised by a unique empirical parameter b. Formulae have also been proposed[90] for the estimation of the average bond lengths $\overline{R}(P-O)$ in the PO_4 tetrahedra, which take into account the number of cations surrounding the oxygen atoms and the distortion of the polyhedron.

Baur's model has narrow limits of applicability and is suitable only for relatively undistorted polyhedra. For example, it does not permit the description of the distortion in the structures of ferroelectrics belonging to the perovskite family, since according to Eqn. (4), one would have to expect the equality of all the isotypical bonds in the perovskite structure, whereas in reality, these bonds are not equivalent. It became clear from subsequent studies that the reason for this is the unsatisfactory linear approximation used for the dependence of the bond valence forces [bond strengths] on interatomic distance.

Pauling[92,93] initiated the use of the non-linear functions $S(R)$ and suggested that metallic and covalent bonds be described by the logarithmic relation

$$R = R_1 - A \ln n, \tag{5}$$

where R_1 is the length of a single bond, n the "bond number" defined as the number of delocalised electron pairs per bond, and A a coefficient (A = 0.30 Å for covalent bonds).

For ionic-covalent bonds, an expression of a similar form was used in the analysis of the interatomic geometry in V_2O_5 crystals as early as 1951.[94] Subsequently, a similar relation was used also to describe the Mo–O bonds.[95,96] The construction of plots of $S(R)$ without their analytical interpretation[97] is based on the concept of electron hybridisation. As a rule, the sums of the valence forces (bond orders) on the cations, determined by Eqn. (5), are close to the formal valences of the central atoms:

$$p\mathrm{M} = \sum_i S_i \simeq V_\mathrm{M}. \tag{6}$$

In the calculation of the Mo–O bond orders from the plot published by Cotton and Wing,[97] it was found that the sum of pMo appreciably exceeds the formal value of 6.

An alternative analytical expression for $S(R)$ was proposed independently by Donnay and Allmann[98] and by Pyatenko.[99] In both cases, the authors assumed that the interatomic interaction in typical inorganic structures obeys a power relation with an exponent $N > 1$ and not Coulomb's law. This approach was formulated in its final form in a study[100] where the analysis of the oxygen polyhedra in 417 reliably elucidated structures permitted the conclusion that all isotypical M–O bonds can be described by unique relations:

$$S_i = (R_i/R_1)^{-N}. \tag{7}$$

The set of empirical parameters R_1 and N was subsequently significantly extended.[101] The deviations of the values of pM calculated by Eqn. (7) from the true values of V_M are very insignificant (up to 5%). The parameters R_1 and N for the M–X bonds with X = O, F, Cl, S, P, or N, have been published.[78]

The principal qualitative feature of the model[100] consists in the fact that it does not require an "ionic" treatment of the valence balance rule and can be extended to any bonds of the ionic-covalent type. The very terms "cation" and "anion" are used not in the "electrostatic" sense but merely as designations reflecting the differences between the more electropositive partner in the chemical bond from the more electronegative one.

It has been established in recent years that the agreement with experiment achieved using the function (7) is ~30–50% worse than that obtainable with the aid of Eqn. (5), which can be written in the form[102–104]

$$S_i = \exp\left[(R_1 - R_i)/K\right], \tag{8}$$

where K and R_1 are empirical constants. The existence of a large set of experimental data, embracing 15371 polyhedra, made it possible to define the values of R_1 for the set of M–X bonds and to propose a method for the estimation of these parameters for other combinations of M and X.[103] The coefficient K was assumed to be constant for all types of bonds (K = 0.37 Å).[103] According to other data,[102,104] this parameter is specific to each set of M–X and varies in the range 0.25–0.48 Å. In view of the significant inequality of the bond lengths in the coordination polyhedron, the use of the coefficient K = 0.37 Å leads to a poorer fulfillment of the requirement for valence balance in structures than the use of values of K specific to each type of M–X bonds.[105] By virtue of the arbitrary selection of the constant of K = 0.37 Å, the empirical coefficients R_1 quoted by Brown and Altermatt[103] have values which are not entirely physically justified despite the acceptable accuracy of the results obtained by Eqn. (8).

1. In the case of polyvalent cations, the coefficients R_1 for their high oxidation states are greater than for their low oxidation states, which is itself doubtful (see also Zachariasen[84]).

2. The character of the variation of the quantities R_1 in the series of isoelectronic cations conflicts with their physical significance, since the smallest values of R_1 correspond to intermediate members of the series.

3. The previously established[100] relation between the position of the cation in the Periodic System and the values of R_1(M–O) is not manifested.

Furthermore, in the proposed method of calculation[103] no difference is drawn between transition metal cations in different spin states although the latter factor affects bond lengths.[106]

The determination of individual values of K for different types of M–X bonds involves certain difficulties, because the parameters R_1 for real structures vary in the range ±(0.015–0.020) Å relative to the statistical mean value found from the analysis of a large set of data for a wide variety of classes of compounds (simple and complex oxides, salt hydrates, complexes with involved organic ligands[105]).

The quantity R_1 depends on the characteristic features of the crystal structure.[104,105] It increases steadily with increase in the number of cations linked to the anion X participating in the M–X bond and also with decrease in their electronegativity. In the structure of hydrates, where the thermal motion of water molecules coordinated to the cation assumes significant importance, the quantity R_1 is, on the contrary, smaller than the statistical mean value. It has been suggested[105] that comparison of the values of R_1 for isotypical bonds in different structures can yield information about the effective charges of the atoms forming the bonds.

In recent years the bond valence force [bond strength] model has found a multiplicity of applications[78,98–112] by virtue of the satisfactory agreement between the results of calculations based on this simple model and experimental data. The conclusions arising from it have been confirmed by quantum-chemical methods.[83]

The model is applicable not only to the solution of traditional problems of structural analysis (including the identification of hydrogen bonds, the determination of the location of the "light" cations of the Li type,[109] the determination of the ratio of two kinds of atoms in the statistical population by the latter of one site,[100] and

the test of the validity of X-ray diffraction analysis[108]), but also to the estimation of the strengths of Lewis acids and bases[108] and the amount of ionic character of bonds.[100] Correlations have also been found between valence forces S and force constants for bond stretching[105] and the coefficients of thermal expansion of crystals.[111] Attempts have been made to use the values of S for the estimation of bond energies.[113]

Statistical studies[104,112,114] have shown that the individual values of S in the TO_4 tetrahedra, where T = Ge, P, V, S, Se, Cr, Mo, or W, obey a simple rule: they lie within the range of values from $V_T/6$ (the mean value $\overline{S}$ in the hypothetical undistorted TO_6 octahedron) and $V_T/3$ (the value of $\overline{S}$ in the hypothetical TO_3 triangle), where V_T is the formal valence of the central atom. Hence the limiting interatomic distances in these polyhedra can be found readily with the aid of Eqn. (8).

series of tetrahedra and pseudotetrahedral complexes with unshared electron pairs and the arithmetical mean values of valence forces of the bonds forming these angles. A similar relation has been found for octahedra.[104,115] Thus the method can be assessed as complementing the Gillespie method[79] for the solution of problems in coordination chemistry which has gained much popularity in recent times.

The bond valence force [bond strength] model has been used in its qualitative aspect [average valence forces determined by Eqn. (1)] for the solution of problems of the stability of crystalline substances and for the systematic treatment of data on polymorphism.[104,116]

We shall now list the principal features of the model.

1. The valence balance rule has a simple topological justification.[105] According to the principle of the superposition of the sum and of its independence of the order in which the summation is carried out, the sums ΣS with respect to all the bonds formed by any atom in the crystal structure must be equal to the formal valence of this atom. The problem thus reduces to the correctness of the determination of the function $S(R)$ and its coefficients.

2. The dependence of the individual valence forces of bonds on the length of the latter is described by an exponential law. The parameters K and R_1 in Eqn. (8) have values determined by the nature of the atoms forming the bond.

3. The "characteristic" bond valence forces (S_0) of isoelectronic cations combined with the same anion depend on the "characteristic" interatomic distances (R_0):

$$R_0 = \rho S_0^{\mu}, \qquad (9)$$

where ρ and μ are empirical constants. The term "characteristic" is applied here to the statistical mean values of R_0 and S_0. Eqn. (1) can be used to determine S_0 for a specified statistical mean coordination number CN_0. Equations of type (9) can apparently be used also for polyvalent cations.

Taking into account the information obtained using the model described above, one can formulate the following definition of the concept of the "bond valence force": bond valence forces are understood as model characteristics of interatomic interactions whose sum with respect to all the bonds formed by the given atom is numerically equal to the degree of oxidation of this atom [the number defining its oxidation state? (Ed. of Translation)].[105]

2. The structure forming role of cations

A trend has arisen in recent years to overestimate the structure-forming function of cations.[80,104,117–124] Whereas previously the analysis of crystal structures was restricted to the consideration of individual chemical bonds between atoms, i.e. to problems of coordination chemistry, nowadays the elucidation of the nature of the formation of the crystalline object as a whole has assumed decisive importance. The concept of the most compact disposition of the largest species, i.e. the largest anions and cations, has helped to some extent in elucidating the characteristics of the formation of crystal structures. However, this "packing" concept loses significance in the case of compounds with "heavy" cations.

There exist two aspects of the solution of the problem of non-bonding intercationic interactions which undoubtedly influence the dynamics of crystal lattices. Firstly, a topological approach, operating with the concept of the cationic matrix (framework, skeleton) has been developing[121] (see also Trunov et al.[104]). A method has been developed within the framework of this approach[117–124] which is based on the indentification of the planes in crystal structures most highly populated by cations. The reflections corresponding to such planes are as a rule most intense on X-ray diffraction patterns. The most compact relative disposition of cations in the planes is achieved when each cation is surrounded simultaneously by six other cations (the so-called "trigonal networks" of the 3^6 type are then formed), but there is also a possibility of "mixed" networks of the $3^3.4^2$ type with triangular and square cells, 4^4 networks with only square cells, and topologically more active networks.

It has also been suggested that individual cations can project from the planes of the networks over distances up to 0.5 Å (which amounts to 15% of the intercationic distance), while the cationic subcell sites are not subdivided as regards chemical "kind", so that vacancies can also correspond to them.[121]

According to Trunov et al.,[104] this approach can be usefully complemented by the analysis of the deformability of the cationic sublattice and the ways in which individual chemical kinds of atoms can alternate in its sites. The method for the identification of cationic motifs is used not only for the traditional classification purposes but also in considering a wide variety of solid-phase transformations, including polymorphic transformations[123] (see also Refs. 41, 46, and 48). It is also used in X-ray diffraction analysis to establish the positions of light anions if the compound includes heavy cations.[117,119]

The other approach to the analysis of the relative disposition of cations, proposed by O'Keeffe and Hyde[125,126] and by Glidewell,[127] is based on the experimentally established relatively small scatter of the "non-bond" intercationic distances when polyhedra are combined via a single common vertex regardless of the nature of the common ligand. A kind of system of "radii" has been developed, whose application ensures a satisfactory fulfillment of the additivity rule when neighbouring polyhedra are linked via a common vertex.[80] For "light" cations (including representatives of the 3*d* group of transition elements), the radii do not exceed 1.7 Å; for example, for sulphur(+6), the radius is 1.45 Å. The corresponding parameters for hexavalent molybdenum (1.90 Å) and tungsten (1.91 Å)[105] fall within the range of values 1.8–2.1 Å characteristic of the lanthanide and other "heavy" cations. When common edges are present in the polyhedra shorter (by 10–15%) intercationic contacts arise. For example, in the case of molybdenum the "intercationic interaction radius" is 1.59 Å.[105]

Thus the characteristic features of the relative disposition of cations in space are determined also by non-bonding interactions, as a result of which in the cations, with their highly developed electron core, the trend to achieve the most uniform environment comprising similar species becomes dominant, which promotes the formation of independent structural types.

We believe that the application of both schemes described above for the analysis of cationic motifs (topological and geometrical), combined with the methods of coordination chemistry (description of bonds and interbond and interligand interactions), will promote the achievement of a qualitatively new level for the consideration of the nature of the crystal structures of inorganic compounds.

3. Characteristic features of the coordination of molybdenum(VI), tungsten(VI), and the lanthanides(III) to oxgyen atoms

The crystal-chemical and stereochemical aspects of the coordination chemistry of molybdenum and tungsten compounds in the state current at the beginning of the 1970s have been described in detail.[128] During the past period, there has been a marked expansion of the number of experimental determinations and an increase in their accuracy.

A statistical survey of data on oxygen-containing molydenum(VI) and tungsten(VI) polyhedra has been carried out.[104,112] In all, information about 383 polyhedra, in which the coordination number of molybdenum varies from 4 to 7, was used. Among the total number of polyhedra, the MoO_4 tetrahedra constitute 48.6%, the MoO_5 pentagonal structures constitute 2.9%, the MoO_6 octahedra constitute 48.0%, and the MoO_7 pentagonal bipyramids constitute 0.5%. This distribution agrees with the frequency of the occurrence of particular coordinations of molydenum(VI) estimated[112] with respect to all known (including isostructural) compounds having a reliably determined coordination with respect to oxygen. The number of double molybdates alone, with heterovalent cations, taken into account in the analysis was more than 500.[104]

The tetrahedral coordination with respect to oxygen, which is so characteristic of molybdenum, is atypical for hexavalent tungsten. The WO_4 tetrahedra constitute only 10% of the total number of polyhedra, the fraction of WO_5 is 4.5%, and the fraction of WO_7 is 0.5%, so that the hexenary WO_6 coordination predominates (85%). Apart from octahedra distorted in different ways, there are also isolated examples of trigonal-prismatic coordination which occurs in similarly constructed double salts (with respect to the anion) of the type La_3WO_6X, where X = Cl_3, Br_3, or BO_3.[105]

The coefficients K and R_1 in Eqn. (8), with the aid of which the bond valence forces are determined, have the following values: K = 0.354 Å and R_1 = 1.905 Å for Mo–O; K = 0.342 Å and R_1 = 1.922 Å for W–O.[105]

The Mo–O bond lengths in the MoO_4 tetrahedra vary in the range from 1.66 to 1.91 Å, while the W–O bond lengths in the WO_4 tetrahedra vary from 1.69 to 1.92 Å. The distribution functions for the individual interatomic distances are themselves characterised by positive asymmetry[104,105] (and resemble "inverted" Morse functions) with a Gaussian "smearing" of the wings of the distributions, but the corresponding valence forces are distributed in accordance with a pseudonormal law. The most probable bond lengths in the tetrahedra are R(Mo–O) = 1.762 Å and R(W–O) = 1.775 Å (they correspond to the maxima in the distribution functions for the corresponding R_i).

The variation of the bond lengths in the tetrahedra under the influence of the "external" cationic environment are described quite satisfactorily[104] by the following expressions:

$$R(\mathrm{Mo-O}) = 1.675 + 0.186\Sigma S_{ext}, \quad (10a)$$

$$R(\mathrm{W-O}) = 1.632 + 0.272\Sigma S_{ext}, \quad (10b)$$

They take into account the contributions S_{ext}, determined from Eqn. (1), of all the "external" cations to which the given oxygen atom is coordinated. Since it is known that in the case of SO_4 tetrahedra the coefficient of ΣS_{ext} is 0.128 Å,[104] one can follow the variation of the T–O bond length in the S→Mo→W series for equal "external" influences. When the upper limit of the bond lengths in tetrahedral anions is exceeded, the coordination number of the central atom increases. This explains the low abundance of tetrahedral groups in the case of WO_4. Furthermore, it follows from Eqns. (10) presented that the formation of the "dimolybdate" groups $[Mo_2O_7]$ from two tetrahedra which are joined via one common oxygen atom, requires the formation of an Mo–O bridge bond whose length is such that it is in practice unlikely, while the formation of "ditungstate" anions appears altogether impossible. Indeed, $[Mo_2O_7]$ groups are stable only in specified instances,[129] which include, for example, the lanthanide hexamolybdates $Ln_2(Mo_2O_7)_3$,[77,112] $MgMo_2O_7$,[130] and $Ce_6(MoO_4)_8(Mo_2O_7)$,[30] which exist within narrow temperature ranges.

The length D of the O–O edges in the MoO_4 tetrahedra is from 2.66 to 3.11 Å, the statistical mean value being 2.882 Å. The distances D(O–O) are linearly related to the corresponding angles α(O–Mo–O) (correlation coefficient 0.82):

$$D(\mathrm{O-O}) = 0.25 + 0.024\alpha(\mathrm{O-Mo-O}),\ \text{Å (Ref.105).}$$

In contrast to the angles α(O–P–O) and α(O–S–O) in PO_4, SO_4, and other polyhedra, whose distortion is well described by the interbond or the non-valence interligand repulsion model,[128] the angles α(O–Mo–O) and α(O–W–O) in the MoO_4 and WO_4 tetrahedra tend to decrease as the bonds connecting these angles are shortened.[104] Under these conditions, additional oxygen atoms from the nearest tetrahedra are frequently included in the coordination sphere of Mo or W; the new atoms tend to occupy the *trans*-positions relative to the shortest Mo–O or W–O bonds in the initial polyhedron and lie over the "centres" of its expanded faces.

This feature of the distortion of the tetrahedra and the relatively high value of the parameter characterising the distance between the cations in the case of Mo and W (see the previous section) prevent the combination of the edges of the MoO_4 and WO_4 tetrahedra with other coordination polyhedra whose central atoms are high-valence ($V_M \geqslant 3$) divalent cations with an ionic radius not exceeding 1 Å. On the other hand, for sulphate ions such combination of edges is fairly typical.

With increase in the coordination number of Mo or W to 5 as a result of the approach to an O atom belonging to a neighbouring polyhedron, the dimers $[Mo_2O_8]$ or $[W_2O_8]$ are frequently formed. The length of both oxygen edges in such dimers is shortened. The pentagons usually have the form of a trigonal bipyramid in which the *trans*-influence of the axial atoms is very marked in agreement, with theory.[72,128] The bipyramids can have common oxygen edges not only with one another but also with other polyhedra.[46]

Contrary to the existing view about the similarity of the MoO_6 and WO_6 octahedra, a statistically reliably established distortion of the 2 + 2 + 2 type (gradation of the Mo–O bond lengths) is characteristic of MoO_6 octahedra.[112] Three equal-intensity maxima at R = 1.707, 1.928, 2.282 Å can be differentiated on a plot of the

R(Mo—O) distribution function. Owing to the non-linearity of the function $S(R)$ and the high degree of distortion of the polyhedra [$D_2(R)$], defined by the relation

$$D_2(R) = \left[\frac{1}{CN}\sum_{i=1}^{CN}(1 - R_i/\overline{R})^2\right]^{\frac{1}{2}}, \quad (11)$$

where $\overline{R}$ is the average bond length in the polyhedron, the arithmetical mean bond length R for the entire set of octahedra, i.e. R_m(Mo—O) = 1.973 Å, significantly exceeds the "undistorted" value R_1 = 1.905 Å. The mean distortion is $D_2(R)$ = 0.118.[112]

The WO_6 octahedra are not subject to similar "characteristic" distortions. Their average distortion is $D_2(R)$ = 0.043 and R_m = 1.940 Å for R_1 = 1.922 Å. This example is very clear, since it shows that the estimates of the size of the cations obtained using "statistical" interatomic distances may not correspond to the experimental data (including data obtained from the formula volumes of isostructural compounds) in the case of highly distorted (to different extents) polyhedra.

The "external form" of the MoO_6 and WO_6 octahedra, determined by the lengths of the oxygen edges, varies, like that of the corresponding tetrahedra,[104] to a smaller extent than all other stereochemical parameters of the polyhedra. However, whereas a unimodal distribution of the D(O—O) distances is characteristic of MoO_4, in the case of MoO_6, with the average value D_m(O—O) = 2.745 Å, a trimodal distribution is observed owing to the shortening of the lengths of oxygen edges common to other polyhedra. Three maxima can be distinguished at 2.615, 2.735, and 2.820 Å, their contributions to the overall distribution of the D(O—O) distances being 19, 35, and 46% respectively.[112] The shortest D(O—O) distances correspond to the common edges. In order to retain the average length D_m(O—O) for the octahedron, it is necessary to increase the length of the "free" edges, which is manifested by the presence of a third maximum on the distribution function curve. A similar phenomenon was also noted for GeO_6 octahedra.[114]

The average length of the edges D(O—O) in the WO_6 octahedra varies within comparatively narrow limits (2.71—2.77 Å), whereas the values of D_i specific to each individual polyhedron vary from 2.38 to 3.35 Å. The reason for this scatter is the shortening of the lengths of the common edges reflected by the appearance on the distribution function curve of a satellite maximum at 2.48 Å and a "compensating" maximum at larger distances: D(O—O) = 3.14 Å. Overall, a distortion of the external form is characteristic of the WO_6 octahedra in which there are six shortened oxygen edges and six lengthened oxygen edges in the *trans*-positions with respect to the former.

There is a strong linear correlation between the angles α(O—W—O) and the arithmetical mean values of the valence forces $\langle S$(W—O)$\rangle$ of the bonds forming this angle:

$$\alpha(\text{O—W—O}) = 51 + 39\langle S(\text{W—O})\rangle \quad (12a)$$

with a variance of ~4°. The α(O—W—O) angles range from 70° to 113°, the most acute of them being based on the common edges of the polyhedra.

A similar relation

$$\alpha(\text{O—Mo—O}) = 62 + 27\langle S(\text{Mo—O})\rangle, \quad (12b)$$

characterised by a correlation coefficient of 0.96, holds also for MoO_6.[112]

Such features of the variation of the stereochemical parameters of the octahedra make it possible to put forward two mutually consistent justifications of the small variability of the lengths of the oxygen edges D(O—O) in the absence of perturbations by additional polyhedra.

1. The increase in the angle between short bonds and the decrease in the angle between long bonds are consistent with the interbond repulsion model[79] and lead (by virtue of trigonometric relations) to similar values of D(O—O) in both cases.

2. As for the tetrahedra, the interligand non-valence interactions tend to "equalise" the lengths of the oxygen edges.

In order to account for the observed distortions of the MoO_6 and WO_6 octahedra, it is also necessary to invoke the closeness of the sums of the valence forces of the Mo—O or W—O bonds in the *trans*-positions to the value 2.0 valence units (v.u.).[104,105] This indicates the mutual dependence of the lengths of such bonds [the calculations are carried out by Eqn. (8)]. Thus in the MoO_6 octahedron the Mo atom is displaced from the centre of the polyhedron towards one of the oxygen edges, whereupon two distances R(Mo—O) are shortened compared with the "ideal" length R_1 = 1.905 Å to the "characteristic" length $R \simeq$ 1.707 Å, two R(Mo—O) distances from the molybdenum atom to the oxygen atoms on the opposite edge are lengthened to 2.282 Å, while the remaining lengths of the Mo—O bonds increase slightly to 1.928 Å. In the WO_6 octahedra, the displacements of the W atom from the centre of the polyhedron are not so marked and the cation can then be shifted not only towards two oxygen atoms forming an edge of the octahedron but also to three oxygen atoms forming one of its faces. The corresponding "short" bonds have the length R(W—O) = 1.76 Å (the W—O bond length in the "ideal" octahedron is about 1.92 Å).

This model of the distortion of the octahedra is fully consistent with the data quoted by Porai-Koshits and Atovmyan[128] and explains satisfactorily the fundamental rules governing the coupling of the MoO_6 or WO_6 octahedra formulated by the above workers[128] from the standpoint of the joint application of the concepts of the bond valence forces, the interbond repulsion and the interligand interactions.

When MoO_6 or WO_6 octahedra are combined with one another, they are grouped in such a way that the displacements of their central atoms from their geometrical centres also correspond to the intercationic repulsion model.

There are so far few experimental data on the coordination of the oxygen atoms around the lanthanide atoms and they are suitable only for a qualitative survey. A broad set of a wide variety of coordination polyhedra with coordination numbers ranging from 6 to 12 is characteristic of the lanthanides.[131] Table 2 presents the "average" coordination numbers found from statistical data for the entire set of structures known to the authors[132] in which the lanthanide atoms are coordinated only to oxygen atoms, including those incorporated in organic complex forming molecules. The "average" coordination numbers in the oxide structures proper, not containing water molecules, are also indicated in the table.[112] As a rule, the coordination number in hydrates is higher approximately by unity than in the anhydrous compounds regardless of the number of H_2O molecules. Table 2 also lists the empirical parameters in Eqn. (8) for the valence forces of the Ln—O bonds.[112]

The lower limit of the Ln—O interatomic distances is determined by the lengths of bonds having the valence force S_{max} = 0.67 v.u. [the values of R(Ln—O) can be determined from Eqn. (8)]. This valence force S_{max} corresponds to the hypothetical situation

where the oxygen atom is surrounded by only three lanthanide cations (and no other atoms). Experimental data indicate the absence of such fragments from the structures. The situation where the O atom is surrounded by Ln atoms in a tetrahedral arrangement is extremely common.[133] $S = 2/4 = 0.5$ v.u. corresponds to this situation. The coordination numbers of the lanthanide cations can then vary from 6 to 8.[105,112] For higher coordination numbers of the lanthanide atoms, such fragments are not formed.

Table 2. The average coordination numbers and parameters of Eqns. (8), (14) and (15) for the Ln–O polyhedra.[112,132]

La	n_f	CN_1	CN_2	CN_3	n_p	K, Å	R_1, Å	K^f, Å	R_1^f, Å	n_p'
La	0	8.68	8.38	8.31	94	0.354 (1)	2.175 (2)	0.310	2.220	122
Ce	1	8.65	8.41	8.20	27	0.363 (3)	2.137 (3)	0.313	2.189	46
Pr	2	8.62	8.07	8.08	43	0.270 (1)	2.214 (2)	0.316	2.172	59
Nd	3	8.48	7.85	7.97	137	0.316 (1)	2.155 (2)	0.319	2.151	172
Sm	5	8.27	7.80	7.74	45	0.339 (2)	2.101 (2)	0.326	2.114	58
Eu	6	8.21	7.40	7.63	25	0.307 (2)	2.120 (2)	0.329	2.098	46
Gd	7	8.19	7.51	7.52	70	0.298 (1)	2.114 (2)	0.332	2.083	86
Tb	8	7.83	7.19	7.40	21	0.250 (1)	2.146 (3)	0.335	2.077	23
Dy	9	7.65	7.70	7.29	26	0.304 (4)	2.080 (2)	0.338	2.046	25
Ho	10	7.40	7.25	7.18	31	0.320 (2)	2.047 (3)	0.341	2.027	48
Er	11	7.32	7.20	7.07	56	0.385 (1)	1.969 (2)	0.345	2.006	79
Tm	12	7.22	6.92	6.95	24	0.334 (6)	2.010 (3)	0.348	1.996	24
Yb	13	7.16	6.72	6.84	58	0.369 (1)	1.965 (2)	0.351	1.981	78
Lu	14	7.12	6.74	6.73	38	0.371 (2)	1.963 (3)	0.354	1.978	45

Note. Adopted notation: n_f = number of f electrons in Ln(III); CN_1 statistical mean coordination number for the set of lanthanide compounds of different classes with Ln–O bonds;[132] CN_2 = ditto for anhydrous oxide compounds;[112] CN_3 = coordination number calculated by Eqn. (13); n_p and n_p' = numbers of polyhedra for which an analysis has been carried out; K, R_1 (Å) = individual values of the parameters of the function (8); K^f, R_1^f = the same parameters calculated by Eqns. (14) and (15).[112]

The variation of the stereochemical parameters of the LnO_n oxygen polyhedra is on the whole described satisfactorily within the framework of Gillespie's method,[79] but in the structures of complex oxides with heavy cations the distortions of the polyhedra are frequently determined by the characteristic features of the intercationic geometry.[119] The abolition of the "gadolinium break" in many series of such compounds,[104] especially for a low content of the lanthanide, is remarkable.

There is a linear relation between the coordination numbers of the lanthanides in anhydrous oxide compounds and the number of f electrons n_f of the Ln^{3+} ion:

$$CN^f = 8.31(1) - 0.11(3)\,n_f \qquad (13)$$

(the correlation coefficient is -0.95). The results of the calculations of the coordination number by Eqn. (13) are presented in Table 2. The parameters K in Eqn. (8), describing the valence forces of the Ln–O bonds, are also involved in a weak linear correlation with the number of f electrons n_f:

$$K^f = 0.310 + 0.003 n_f. \qquad (14)$$

On the other hand, if one uses the values of K^f calculated by Eqn. (14) and the coefficients R_1^f are determined from the experimental interatomic distances R(Ln–O), it is found that the coefficients R_1^f are related to n_f:

$$R_1^f = 2.220\,(6) - 0.027\,(9)\,n_f^{0.85(3)} \qquad (15)$$

(the correlation coefficient is -0.9998). The values of K^f and R_1^f calculated by Eqns. (14) and (15) are also listed in Table 2. Using the equation

$$R_0 = R_1^f - K^f \ln S_0, \qquad (16)$$

it is possible to estimate with their aid the average interatomic distances R_0 and the permissible limits of the variation of the Ln–O bond lengths for any coordination numbers of the lanthanide atoms. This requires the determination by Eqn. (1) of the average bond valence force S_0 for the corresponding coordination of the lanthanide or the substitution in Eqn. (16) of the "critical" valence force S_{max} quoted above. In the calculation of the unit cell parameters of compounds by the interpolation or extrapolation methods,[105] a more reliable procedure involves the use of Ln–O bond lengths calculated by Eqn. (16) rather than the ionic radii.[106]

The set of data presented above, characterising the features of the stereochemistry of molybdenum(VI), tungsten(VI), and the lanthanides(III) in the structures of oxide compounds, makes it possible to develop a crystal-chemical approach to the explanation of the chemical compositions, structures, and properties of the crystalline phases in the $Ln_2O_3-MoO_3$ and $Ln_2O_3-WO_3$ systems.

III. Chemical compositions of the compounds formed in the $Ln_2O_3-EO_3$ systems

When molybdenum and tungsten polyhedra are condensed into finite or infinite formations (dimers, strips, layers, etc.), the chemical composition of the latter is determined by the coordination numbers of the central atoms in the initial polyhedral "seeds" and by the way in which they are combined. As regards lanthanide cations, in the presence of a high content of the lanthanide in the oxide one may expect, with a high degree of probability, the stabilisation of the cationic tetrahedra Ln_4O around the oxygen atoms not involved in the formation of the $[MoO_n]$ and $[WO_n]$ groups. The Ln_4O tetrahedra can also be combined with one another. On combining different structural units subject to the condition that the overall electroneutrality of the model crystal is maintained, one may predict the formation of the corresponding compounds.[112] From the set of hypothetical formations, it is essential to select those which are impossible or unlikely on the basis of the known stereochemical and statistical data. Certain limitations are also imposed by the functional economy rule,[104] indicating the formation of stable crystalline structures from a minimum number of fragments with fundamentally different structures.

The only possible type of group in the octahedral coordination of Mo and W atoms when the octahedra are isolated from one another is $[EO_6]$. The $[EO_5]$ fragment can be formed in several ways, the first of which involves the isolation of the EO_5 pentagons. Two other ways reduce to the sharing of elements of the octahedra: two EO_6 polyhedra are either linked in pairs via the edges or the oxygen vertices of each octahedron are shared with two neighbouring ones: $[EO_5] = EO_{4/1}O_{2/2}$. In the latter case, an additional limitation arises from the requirement that the "bridging" oxygen atoms be located in the *cis*-positions relative to one another[128] (see also

Efremov[105]). There are also several ways of organising the $[EO_4]$ fragment. Such fragments can consist of EO_4 tetrahedra isolated from one another, paired pentagons, or chains formed by the latter, i.e. $[EO_5] = EO_{3/1}O_{2/2}$, and finally systems made up of octahedra combined with one another via the four oxygen vertices of each: $[EO_4] = EO_{2/1}O_{4/2}$. In the latter case, there is a possibility of the formation of planar layers in which each polyhedron is linked to four neighbouring ones via common vertices, the formation of zig-zag chains in which the oxygen edges of the octahedra are shared, and the formation of infinite strips in which each octahedron is linked to two neighbouring ones via vertices and with one neighbouring one via a common edge.

Naturally, when the crystal structure contains more than one crystallographic species E (E = Mo, W), the composition or structural characteristics of the fragments $[EO_n]$ can be more varied. For example, the $[E_2O_7]$ fragment can be obtained not only by the sharing of the oxygen vertices of a pair of tetrahedra (which is unlikely in the case of MoO_4 and impossible in the case of WO_4) but also as a result of the combination of the EO_4 tetrahedra and EO_6 octahedra. The overall formula $[EO_4]$ can be a result of the coupling of four EO_6 octahedra to give an isolated tetramer: $[(EO_{3/1}O_{2/2}O_{1/3}.EO_{2/1}O_{2/2}O_{2/3})_2]$.[104] An increase in the complexity of the fragment reduces the probability of its existence.

We examined above the ways in which oxygen atoms are incorporated in the $[EO_n]$ fragments. In addition, oxygen atoms can be linked to the lanthanide cations only (at least four such cations) and can form the $[Ln_qO]$ fragments. The simplest of these is the tetrahedron $[Ln_4O]$. It was noted above that the E = Mo or W cations have "non-bonding intercationic interaction radii" close to those of the lanthanides. This factor promotes the formation of the structures of lanthanide molybdates and tungstates $Ln_pE_mO_n$, where $p:m \geqslant 0.67$, which are fluorite-like or are topologically similar to fluorite.

The composition of the $[Ln_qO]$ fragments is determined by the method in which the $[Ln_4O]$ tetrahedra are joined together and by the empirical crystal-chemical rules. If the numbers of tetrahedra linked to one another in each direction in space are designated by *a*, *b*, and *c*, then the general formula of the fragment assumes the form $[Ln_{(1+a+b+c+ab+bc+ca+abc)/2abc}O]$. The valence balance rule precludes the formation of a layer infinite in two directions with a thickness corresponding to two $[Ln_4O]$ tetrahedra if Ln is in the +3 oxidation state. On the other hand, the layer with $a = b = \infty$ and $c = 1$ and with the composition [LnO] can exist. An element of this layer is an infinite column having the composition $[Ln_2O]$ with the parameters $a = \infty$, $b = c = 1$. The "double" $[Ln_3O_2]$ column with $a = \infty$, $b = 2$, and $c = 1$ is also consistent with the "economy rule". More complex ways of joining together the $[Ln_4O]$ tetrahedra lead to a considerable infringement of the economy rule and can therefore be disregarded.

We shall now consider the simplest combinations in which the anionic fragments $[EO_n]$, the cationic fragments $[Ln_qO]$, and the "free" Ln species are in proportions ensuring the overall electroneutrality of the compound. The results of such studies are presented in Table 3.[112] These data can be usefully compared with those in Table 1, where the known structural types of the binary compounds in the $Ln_2O_3-EO_3$ systems are listed. The chemical formulae of the "model" compounds make it possible to describe the majority of the phases observed in the systems. The compounds in which the functional simplicity of the structural unit is combined with the "crystallographic" ratios of the stoichiometric coefficients in the chemical formulae occur most widely and exhibit the maximum structural variety and a high thermal stability. In such cases the anion-forming elements E can form, together with the Ln cations, stable cationic structural frameworks and together with their immediate oxygen environment can play, at the same time, the role of bulky units generating the structural motif. For example, the EO_6 octahedra in the Dn_2EO_6 structures are incorporated in the cationic framework (type III) and also form two-layer arrangements of networks with trigonal 3^6 (type V), square 4^4 (type IV), and mixed $3^3.4^2$ (type VI) cells.[41]

Table 3. Models of the structures of the phases in the $Ln_2O_3-EO_3$ systems.[112]

Anion	Cation		
	Ln^{3+}	$[Ln_2O]^{4+}$	$[LnO]^{+}$
$[EO_6]^{6-}$	Ln_2EO_6 1:1 4	$(Ln_2O)_3(EO_6)_2$ 3:2 +	$(LnO)_6(EO_6)$ 3:1 1
$[E_2O_{11}]^{10-}$	$Ln_{10}[E_2O_{11}]_3$ 5:6 + (?)	$(Ln_2O)_5(E_2O_{11})_2$ 5:4 —	$(LnO)_{10}(E_2O_{11})$ 5:2 1
$[EO_5]^{4-}$	$Ln_4(EO_5)_3$ 2:3 1	$(Ln_2O)(EO_5)$ 1:1 2	$(LnO)_4(EO_5)$ 2:1 +
$[E_2O_9]^{6-}$	$Ln_2E_2O_9$ 1:2 1	$(Ln_2O)_3(E_2O_9)_2$ 3:4 —	$(LnO)_6(E_2O_9)$ 3:2 +
$[EO_4]^{2-}$	$Ln_2(EO_4)_3$ 1:3 5	$(Ln_2O)(EO_4)_2$ 1:2 +	$(LnO)_2(EO_4)$ 1:1 3
$[E_2O_7]^{2-}$	$Ln_2(E_2O_7)_3$ 1:6 1	$(Ln_2O)(E_2O_7)_2$ 1:4 0	$(LnO)_2(E_2O_7)$ 1:2 0

Note. The oxide ratio $nLn_2O_3:mEO_3$ is indicated at each position in the second row. The numeral in the third row denotes the number of elucidated structural types: the + sign indicates the possibility of the formation of the given structure and the symbol 0 indicates its impossibility. A dash means that the compound has not been detected.

In another characteristic family $Ln_2(EO_4)_3$ the isolated tetrahedral anions EO_4 either play an independent structure-forming role if lanthanides at the end of the series form part of the composition of the compounds or, together with the initial members of the series, form a fluorite-like cationic framework in several varieties of the scheelite structure.[71]

The proposed modelling procedure can be extended to compounds with more complex chemical composition containing additional cations.[104,105] By analogy with the science of living nature, one can introduce the concept of the "crystal-chemical groove",[112] which indicates the possibility of the occurrence of a particular crystal structure depending on the individual features of inorganic "building units".

IV. Structure and properties

The physicochemical and certain other structure-dependent properties of compounds in the $Ln_2O_3-EO_3$ systems are examined below. The existing information about the structure of these compounds can be subdivided into four groups of facts.

1. "Neutral" lanthanide molybdates and tungstates, having the same composition $Ln_2(EO_4)_3$ as other compounds with tetrahedral anions whose central atoms E belong to Group VI of the Periodic System, are formed in all the systems.[134]

2. All the lanthanides form the compounds Ln_2EO_6. Similar lanthanide oxytellurates have been described.[135]

3. In the regions corresponding to systems with a high Ln_2O_3 content, phases with a fluorite-like structure are formed.

4. In the $Ln_2O_3-EO_3$ systems, there is a large group of compounds of different composition in the formation of which only a limited number of representatives of the lanthanide series participate.

1. The polymorphism of $Ln_2(EO_4)_3$

In terms of their physicochemical properties, the compounds $Ln_2(EO_4)_3$, can be divided into three main groups. In the so-called *C*, *L*, and *A* families, the oxygen coordination number of the lanthanide cation is 6, 7, and 8 respectively, increasing with increase in the size of the lanthanide. The properties of the molybdates and tungstates vary in parallel. An exception is the absence from $Ln_2(WO_4)_3$ of structures with a senary oxygen coordination of the lanthanide.

As a consequence of the "lanthanide" contraction, the formula volume (V/Z) of compounds having similar structures decreases smoothly in each group with increase in the atomic number of the lanthanide. The morphotropic transition to the next group is accompanied by an abrupt increase in V/Z, which is due to the different numbers and sizes of the vacancies in the frameworks of the different structures:

$$\square Ln_2^{[8]}(EO_4)_3, \quad (A)$$
$$\square_2 Ln_2^{[7]}(EO_4)_3, \quad (L)$$
$$\square_4 Ln_2^{[6]}(EO_4)_3, \quad (C)$$

The numerals in square brackets denote in this instance the coordination number of the Ln atom and the symbol □ represents a vacant site in the cationic framework.

The lattice parameters and the values of V/Z vary smoothly without the "gadolinium break". With increase in the atomic number of the lanthanide, the melting points of the compounds (with the exception of cerium compounds) increase and the temperatures of the transitions to the higher-temperature modifications fall, which agrees with the variation of the coordination number in the series of lanthanides (Table 2). In addition, the upper limit of the stability of compounds with a coordination number of 6 for lanthanides at the end of the series should increase also as a consequence of the additional stabilisation of the LnO_6 octahedra in the ideally balanced *C*-type structure at high temperatures[104] (Fig. 2). The sequence of structural rearrangements occurring on heating corresponds to the rule that the degree of balance in the structure improves, which is expressed qualitatively by the decrease in the quantities $D_2(\overline{S})$, determined by Eqn. (11) for values of pO calculated by Eqn. (2).[104]

Within the framework of one structural group of compounds $Ln_2(EO_4)_3$, the polymorphic transitions can be classified as displacements or ordering processes. The displacements entail a gain in the degree of occupation of the crystal space, for example $C \rightarrow C1$, $L \rightarrow L1$. The simplicity of the organisation of the higher-temperature "undistorted" modification and its high symmetry permit several equivalent routes to the deformation of the structure. This is a necessary condition for the manifestation by the crystals of the properties of ferroelastic materials and, following the loss of symmetry centres, also of ferroelectric materials. Statistical data show that a high symmetry of the local environment is not characteristic of the tetrahedral MoO_4 anions at the usual temperatures.[105,112]

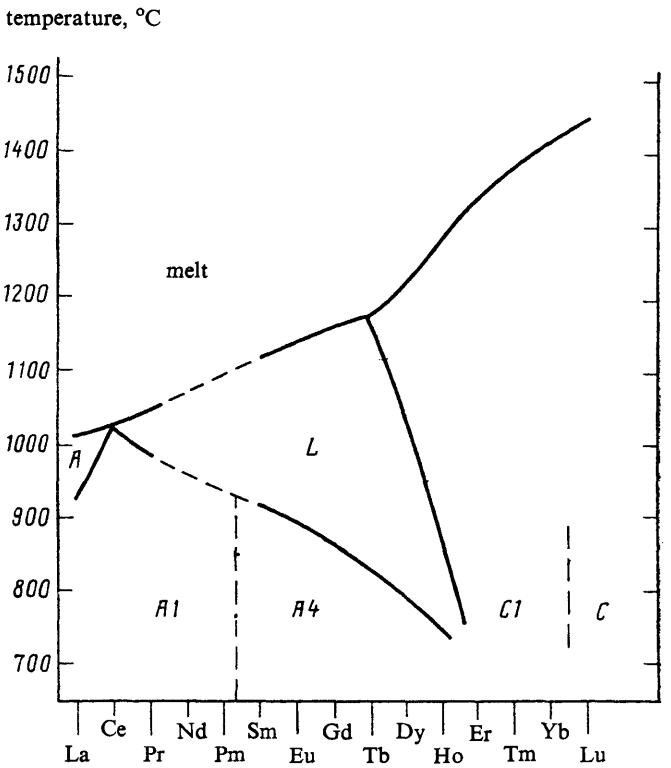


Figure 2. Temperature ranges corresponding to the existence of the polymorphic modifications of $Ln_2(MoO_4)_3$.

Another cause of such displacements of atoms relative to the initial "high temperature" structure is the endeavour by the hexavalent molybdenum and especially tungsten to increase their coordination number when the EO_4 tetrahedra are non-uniformly surrounded by highly charged cations, which is reflected in Eqns. (10). For example, the coordination number of 2/3 of the W atoms in europium tungstate (type A3) increases to 5.[62]

The next type of transformations occurring within the framework of a single structural base involves the ordering of species of different kinds, including vacancies. It proceeds via a diffusion mechanism, certain crystallographic directions proving preferable.

In practice it is frequently possible to obtain structures ordered in different ways. The scheelite-like phases (the *A* family) may serve as an example. The type of ordering can depend also on the way in which the phase is obtained, or on its previous history, and on the presence of impurity atoms in the compound.

2. Polymorphism of Ln_2EO_6

The proposed mechanism of the polymorphism is a result of systematic studies.[27,41–52] Analysis of the morphotropic transitions in this family makes it possible to discover the principal features of the variation of the structures of the most stable modifications (Fig. 3).

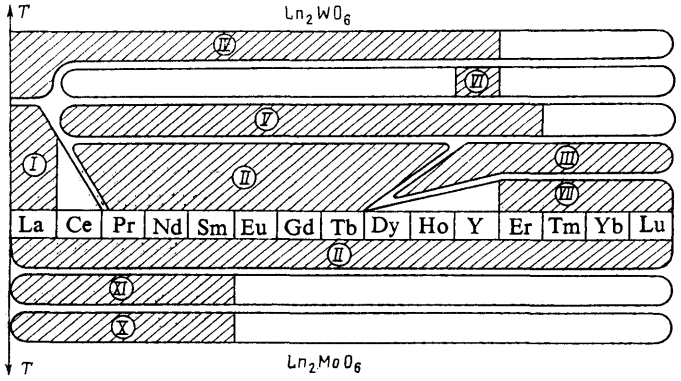


Figure 3. Schematic illustration of the polymorphism of Ln_2EO_6.

The change in the oxygen coordination number in the series of lanthanide cations is insignificant, the coordination number being in the range 8–7, decreasing from La to Lu. In structures of the intermediate members of the series, both coordination numbers occur. The coordination number of the anion-forming element (E = Mo, W) in this series show a tendency to increase from 4 (type X), through 5 (type II), to 6 (types III–VII). Lower coordination numbers are more characteristic of molybdenum in oxymolybdates than of tungsten in oxytungstates. On passing from oxymolybdates to oxytungstates in the La–Lu series, it is possible to identify changes in the structures of the compounds in which the degree of the mutual binding of the cationic tetrahedra $[Ln_4O]$—the residual units of the parent fluorite structure—is reduced. This concerns the following transitions: two-dimensionally infinite [LnO] layer in X→double $[Ln_3O_2]$ strip in II→infinite $[Ln_2O]$ column in VII→Ln^{3+} cation not involved in the formation of the $[Ln_qO]$ fragment in III–VI.

Fluorite-like cationic frameworks are characteristic of the structures of the majority of the low-temperature modifications, while the structures of the known high-temperature forms IV–VI are determined by the arrangement of large octahedral WO_6 anions which are isolated from one another.

The phase transitions between different modifications of Ln_2EO_6 are reconstructive. The reversible and readily occurring structural transformations V⇄VI⇄IV reduce to successive displacements of part of the WO_6 oxy-anions within the framework of the layer and to slight displacements of the lanthanide cations.[41] It is remarkable that all three high-temperature forms of oxytungstates are identical, whereas the low-temperature polymorphic modifications have a centrosymmetrical structure. The interconversions of the low-temperature modifications proceed via more complex pathways but they are also imagined to be subdivided into a sequence of "elementary" movements of the lanthanide cations and the elements E in steps not exceeding the typical intercationic distance of 4 Å.[46,48]

In each group of isostructural compounds, an increasing number of signs foreshadowing a change in the structural type, involving an increase in strain in contacts of the type O...O or M...M′ (M = cation), are observed as the extreme members of the series are approached. The significant shortening of one of the Ln...W edge contacts in the WO_6 and LnO_7 polyhedra on passing to the lanthanides at the end of the series is in fact responsible for the widening of the temperature range corresponding to the existence of form III with a coordination number of 8 instead of the widening of the region corresponding to the stability of structures of type V where there are seven nearest oxygen atoms in the environment of each Ln cation of both kinds.

An important structural characteristic of the majority of polymorphic modifications of Ln_2EO_6 is the presence in the latter of at least two crystallographic kinds of lanthanide atoms which in a number of instances are involved in different types of oxygen coordination. This makes it possible to "regulate" the extent of the temperature ranges corresponding to the stability of the phases on transition from the double oxides proper to the solid solutions based on them.[27]

3. Fluorite-like compounds in the $Ln_2O_3–EO_3$ systems

The most contradictory interpretation of the phase relations in the $Ln_2O_3–EO_3$ systems is in the region of a high content of the lanthanide components (in excess of 60 mol%). Compounds of several types are formed whose common feature is the involvement of fluorite (CaF_2) as the structural prototype. Whereas an octonary oxygen coordination is characteristic of the lanthanides (especially those at the beginning of the series) in the oxygen compounds (Table 2), the occurrence of coordination numbers ranging from 4 to 6 for Mo and W requires a definite rearrangement of the initial fluorite structure in order to ensure an environment characteristic of these elements. This can entail the displacements of the anions from the positions at the centres of the cationic tetrahedra to the triangular faces of the latter, the formation of anionic vacancies, and local displacements of the atoms in the non-ordered phases.

In examining the correspondence between the chemical composition of the phase and its crystal-chemical nature, one can imagine several situations.

1. Atoms of each kind wholly populate particular regular systems of points in the structures of the compounds. With the exception of the special cases of "subtraction phases" or "interstitial phases" where the ordering is complete, compounds are formed with a distinct stoichiometry and fairly narrow regions of homogeneity.

2. Anionic disordering takes place when the number of sites for the accommodation of anions, determined by the multiplicity of the regular system of points in the space group of the crystal, exceeds the actual number of anions corresponding to the chemical formula of the compound. Owing to the absence of some of the anions from the structure as a consequence of thermal motion, there is a

possibility of the migration of the remaining anions between crystallographic positions belonging to the same regular system of points. This mechanism is most probable at high temperatures. When the anions and vacancies are distributed statistically among the same positions, situations where cations of different kinds (Ln and E) are involved in oxygen coordination characteristic of them are entirely realistic.

3. Finally, at very high temperatures (in excess of 1400 °C), the crystal-chemical individuality of the cations is abolished owing to the thermal motion of the atoms, as a result of which they become statistically distributed among the sites of the initial prototype structure. The usual crystal-chemical rules which hold at the normal temperatures, apparently lose their significance under these conditions (Fig. 1).

Among the large number of "fluorite-like" phases listed in Table 1, only the structures of Ln_6EO_{12} (rhombohedral form) and $Ln_{10}E_2O_{21}$ have been reliably characterised. Furthermore, studies at high temperatures have shown that the compounds Ln_6EO_{12} give rise to broad regions of homogeneity based on the cubic fluorite structure in the vicinity of the melting points. The formation of such phases at low temperatures (1000–1200 °C) in the initial stages of the synthesis can apparently be attributed to the characteristic features of the solid-phase reactions in systems the composition of the components of which include cations with similar "radii of intercationic interactions through bonds". Such labile phases can be assessed as a kind of intermediate "activated complexes". For example, the cubic oxytungstate La_6WO_{12} in the $La_2O_3-WO_3$ system is thermodynamically stable only above 1900 °C (Fig. 1), but the synthesis from the oxides at temperatures below 1400 °C affords, as a result of the annealing of the reaction mixture for 5–20 h, a single-phase product characterised by a similar X-ray diffraction pattern.

Compounds having the approximate composition $7Ln_2O_3.4EO_3$ are in reality mixtures of phases ordered in different ways and having similar stoichiometries and fairly complex superstructures[29] like the phases in the $Ce_2O_3-CeO_2$ system.[136]

4. Compounds having other compositions

The stereochemical differences between the molybdenum and tungsten atoms coordinated to oxygen atoms begin to have an appreciable effect in the structures of lanthanide polymolybdates and polytungstates, i.e. compounds having the composition $Ln_2O_3.nEO_3$, where $n > 3$. The chemical compositions of polytungstates and polymolybdates are different. The only type of polytungstates ($Ln_{10}W_{22}O_{81}$) has a "bronzoid" structure, which consists of a complex interlinked set of WO_n pentagons, hexagons, and heptagons, each of which is joined to two similar formations via common axial oxygen vertices. This structure shows a definite similarity to that of polytantalates.[76]

Polymolybdates unexpectedly have structures which incorporate dimerised tetrahedra. The $[Mo_2O_7]$ groups can be very remote from other Mo–O anions. The temperature ranges corresponding to the stability of the compounds $Ln_2(Mo_2O_7)_3$, formed under equilibrium conditions at temperatures of the order of 650–720 °C, are extremely narrow (of the order of 30–70 °C).[77] An interesting feature of these systems is the ease of hydration of the quenched specimens (they are quenched to prevent their decomposition on cooling). Such ease is caused by the presence in their structure of large cavities combined into a single system of channels.[76] The trapped water molecules increase the coordination number of the lanthanide atoms from 8 to 9, which stabilises the structure of the monohydrate. The large hydrated crystals can be stored without change for at least 15 years.[76] On heating, the coordinated water is removed at about 280 °C, after which the compound decomposes at about 450 °C into the tetramolybdate and MoO_3; on further increase in temperature, it is reformed but this time in the region of its thermodynamic stability.[112]

In the structures of heavy lanthanide tetramolybdates $Ln_2Mo_4O_{15}$, the dimolybdate ions no longer play an independent role. They are built up to pentagonal formations by combining with neighbouring MoO_4 tetrahedra, which ultimately leads to the appearance of the $[Mo_4O_{15}]$ fragment.[75] The tetramolybdates of the lanthanides in the middle of the series contain isolated MoO_4 tetrahedra and complex polymeric fragments $[Mo_8O_{29}]$ made up of MoO_n tetrahedra, pentagons, and octahedra.[76] The formation of tetramolybdates in the structures of which there are isolated MoO_4 groups and polymer chains having the composition $[Mo_2O_7]$, made up of tetrahedra and octahedra, is characteristic of the lanthanides at the beginning of the series.[74]

On the other hand, tungstates are more widely represented when the ratios of the initial oxides are $Ln_2O_3:EO_3 > 1:3$. They contain WO_6 octahedral groups. This fact agrees well with the views described above concerning the greater tendency of tungsten(VI) compared with molybdenum(VI) to form compounds with high degrees of coordination under the influence of the "external" cationic environment. The great variety of ways in which the WO_6 octahedra can be distorted and of the types of their bonding also promotes the formation of different phases in the systems (Fig. 1).

The changes in the temperature ranges corresponding to the stability of such structures are also correlated with the degree of distortion of their constituent coordination polyhedra.

V. Conclusion

Despite the great variety of types of crystal structures of lanthanide molybdates and tungstates and the wide range of variation of the coordination numbers of E (from 4 to 7) and Ln (from 6 to 11), there is a profound relationship between the coordination numbers of the cations and their relative contents in specific structures.[112] Fig. 4 presents the changes in the "average" bond valence forces $\overline{S}_M$ in the structures of compounds of the lanthanides at the beginning, in the middle, and at the end of the series. The weighted mean value of the individual S, found by Eqn. (1), was used as $\overline{S}_M$:

$$\overline{S}_M = \left[\sum_i (n_i V_{M_i})/CN_i\right] \Big/ \sum_i n_i,$$

where V_{M_i}, CN_i, and n_i are respectively the formal valence, the coordination number, and the multiplicity of the position in the structure of each of the crystallographically different kinds of cations regardless of their chemical nature. The "generalised oxygen index" α, defined as the ratio of the number of oxygen atoms in the chemical formula of the oxide to the total number of cations, has been plotted along the abscissa axis in Fig. 4. For $Ln_pE_mO_n$, index α is equal to the ratio $n/(p+m)$; in particular, $\alpha = 2.0$ for Ln_2EO_6. The use of the index α makes it possible to compare the properties of compounds having different compositions formed in a single physicochemical system.[112]

The character of the variation of $\overline{S}_M$ with α, similar to that illustrated in Fig. 4, has been observed[112] for a wide variety of pseudobinary systems with several intermediate compounds having

known crystal structures, including compounds of the type $M_2EO_4-Ln_2(EO_4)_3$, where M is an alkali metal ranging from Li to Cs. When the compound forms several polymorphic modifications, the deviations of $\bar{S}_M$ for the high-temperature forms from the straight line joining the values of $\bar{S}_M$ for the initial components diminish.

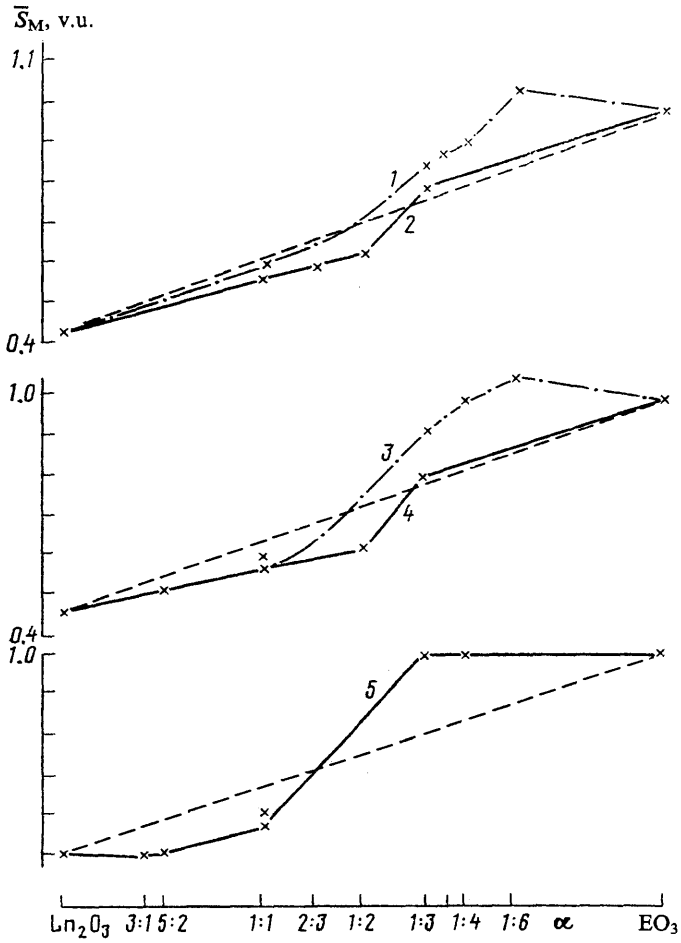


Figure 4. Variation of the quantities $\bar{S}_M$ with the oxygen index α in the structures of compounds formed in different systems: *1*, $Ce_2O_3-MoO_3$; *2*, $Nd_2O_3-WO_3$; *3*, $Sm_2O_3-MoO_3$; *4*, $Eu_2O_3-WO_3$; *5*, $Y_2O_3-WO_3$.

If the composition of the system components includes cations with very different electronegativities, then the relations considered usually becomes S-shaped (Fig. 4). On the other hand, in the case of salt systems of the type $M_2EO_4-L_2(EO_4)_3$, the curves are monotonic.

The dependence on α of the coordination numbers and the values of R_1^E averaged for cations of each kind are also smooth (Fig. 5):[104]

$$R_1^E = R_1^0 + K\ln\left[\left(\sum_{i=1}^{CN} S_i^0\right)\Big/ V_M\right],$$

where R_1^0 is the "statistical mean" value of the empirical parameter from Eqn. (8) and S_1^0 are the valence forces calculated with its aid.

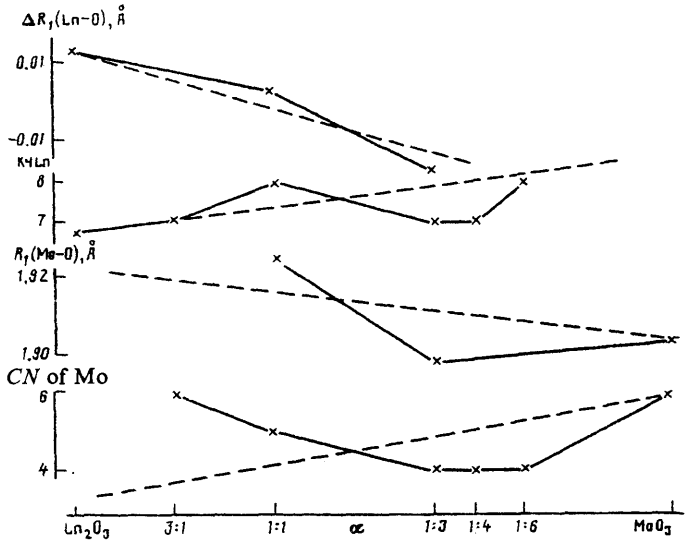


Figure 5. Dependence of the average coordination numbers and the values of R_1 in the structures of compounds of the lanthanides in the middle of the series (molybdates) on the oxygen index.

Presumably the curves illustrated in Figs. 4 and 5 reflect the competition between the cations for the fraction of bond electron density supplied by the anions. It therefore appears useful to consider jointly the results obtained using both bond valence force models as well as other methods of theoretical and experimental chemistry for a wide range of systems. This might promote a more clear-cut establishment of the limits of applicability of the valence force model which has a high predictive power. For example, by introducing hypotheses concerning the alternation of cations and concerning the intercationic distances in the Nd_2MoO_6 structure, it proved possible to determine theoretically the geometrical characteristics of the NdO_8 and MoO_4 polyhedra with approximately the same accuracy as in the experiment.[51]

In our view, the data described in this review will undoubtedly prove useful in the computer modelling of the structure of inorganic oxide compounds.

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Structure of the uncharged, anionic, and cationic forms of aminoalkylcarboxylic and aminoalkylphosphonic complexones

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ABSTRACT. This review is concerned with an analysis of the structure of aminocarboxylic and aminophosphonic acids from the data of X-ray diffraction studies. Monoamino and diamino (also triamino) complexones, the prototropic tautomerism of complexones, and the structural characteristics of their hydrohalides are examined successively.

Contents

I.	Introduction	643
II.	Main structural features of complexones	645
III.	Structure of monoamino complexones	647
IV.	Structure of diamino and triamino complexones	652
V.	Prototropic tautomerism in aminocarboxylic complexones	656
VI.	Structural features of hydrohalides of complexones	659
VII.	Conclusion	660

I. Introduction

In 1936 the company "IG Farbenindustrie" started the manufacture of two products used as water softening agents—Trilon A (nitrilotriacetic acid) and Trilon B (the disodium salt of ethylenediaminetetraacetic acid). These were the first complexones. However, complexones only gained wide acceptance at the end of the 1940s and beginning of the 1950s when their use as complexometric titrating agents for the approximate analysis of virtually all metal cations and many anions was proposed, which gave rise to the current revolution in analytical chemistry.

Schwarzenbach, Kampitsch, and Steiner[1] proposed the term "complexone". Originally it was only applied to polyaminopolycarboxylic acids that have a well-defined tendency to undergo polydentate coordination with metals.

At the present time the term "complexone" refers not only to polyaminopolycarboxylic acids ("classical" complexones) but also to compounds that combine any other basic (S and P atoms, $\rangle C-H$ or $\rangle C-N\langle$ groups) and acidic (phosphonic, arsonic, or sulphonic) sites ("modified" complexones).

In this review only aminocarboxylic and aminophosphonic complexones, whose structure has been studied much more extensively than the structure of other classes of complexones, will be examined. Replacement of carboxyl groups of methylphosphonic groups leads to considerable changes in not only the properties but also the stereochemistry of these compounds. Nevertheless, in the structure of complexones that differ in composition certain common features are retained in many cases, and the present review is to a greater extent devoted to identifying these features. From this point of view there is a discussion of intra- and inter-molecular hydrogen bonds, which play a significant role in the crystal chemistry of all complexones.

During the last ten years the practical application of complexones has extended far beyond the limits of analytical chemistry. They are used anywhere where it is necessary to eliminate the deleterious effect of a metal or, conversely, to introduce a metal into a given system—in the chemical, gas, or petroleum industries, in electrolytic metallurgy, the film industry, power engineering, building, applied bioinorganics, the food industry, agriculture, and in medicine.

The main characteristics of complexones as ligands, making them effective in binding cations and as a result giving rise to their wide popularity in so many different areas, lies in their combination of flexibility and given geometric limitations in coordination, which differ according to the composition of the complexone. The strength of the complexes formed by them is determined, on the one hand, by the considerable covalent nature of the bonds with the metal (namely, by the nature of the active sites of the complexone together with the electronic structure of the metal), and on the other hand by the complementarity of the ligand shape of the complexone with the corresponding cation, i.e., a purely geometric factor. This latter circumstance dictates the importance of studying the stereochemistry of complexones (also metal complexonates).

In the USSR studies on the synthesis of complexones and metal complexonates were started in the 1950s and their systematic structural analysis was initiated in about 1970 [by the group led by T N Polynova at the Chemistry Department of Moscow State University together with the Institute of General and Inorganic Chemistry, USSR Academy of Sciences and by L M Shkol'nikova's group at the All-Union Scientific-Research Institute of Chemical Reagents and Specially Pure Chemicals (VNII IREA)].

On the whole, the structural data on metal complexonates are considerably more abundant than that for complexones themselves. However, even the latter include more than 50 structural studies (two thirds of which have been carried out in the USSR), so that an examination of the results of these studies on the basis of a single approach is now suitable and timely.

The name and standard notation of the aminocarboxylic and aminophosphonic complexes studied are given in Table 1. References to the original X-ray diffraction studies of these compounds are also given there.

Table 1. List of complexones studied.

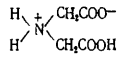
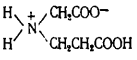
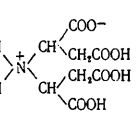
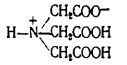
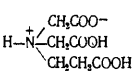
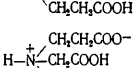
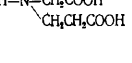
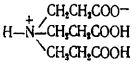
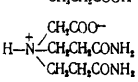
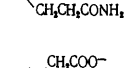
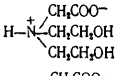
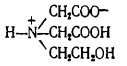
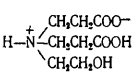
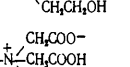
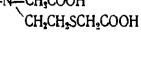
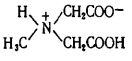
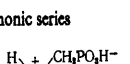
Name of compound	Standard notation	Structural formula	Refs.
Monoaminoalkylcarboxylic series			
Iminodiacetic acid	H_2ida		[2, 3]
Glycinopropionic acid dihydrate	$H_2gp \cdot 2H_2O$		[4]
Iminodisuccinic acid monohydrate	$H_4ids \cdot H_2O$		[5]
Nitrilotriacetic acid	H_3nta		[6]
Nitrilopropionic diacetic acid	H_3npda		[4]
Nitrilodipropionic acetic acid	H_3ndpa		[4]
Nitrilotripropionic acid	H_3ntp		[7]
Nitrilodipropionamidomonoacetic acid	$Hndpma$		[8]
Diethanolglycine	$Hdeg$		[9]
β-Hydroxyethyliminodiacetic acid	$\beta\text{-}H_3heida$		[10]
β-Hydroxyethyliminodipropionic acid	$\beta\text{-}H_3heidp$		[11]
Mercaptoethylaminotriacetic acid monohydrate	$H_3meata \times H_2O$		[12]
Methyliminodiacetic acid	H_2mida		[13]
Monoaminoalkylphosphonic series			
Phosphonomethylglycine	H_3phmg		[14]
Phosphonomethylalanine	H_3phma		[15]
Iminodimethylphosphonic acid	H_4idph		[16]
Phosphonomethyliminodiacetic acid	$H_4phmida$		[14]
Glycinodimethyl phosphonic acid dihydrate	$H_5gdph \times 2H_2O$		[15]

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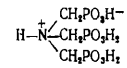
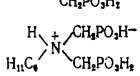
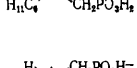
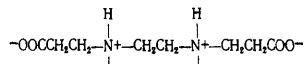
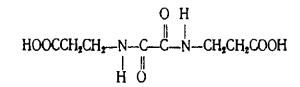
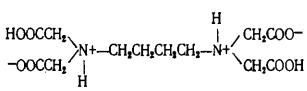
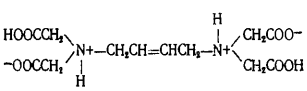
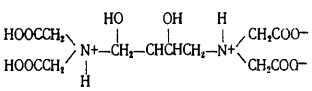
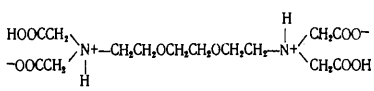
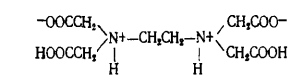
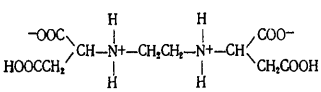
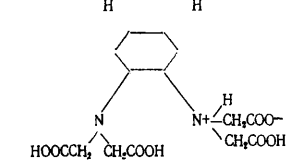
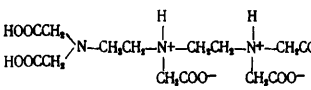
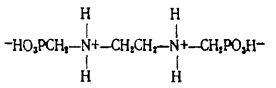
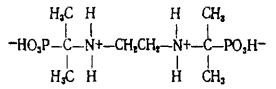
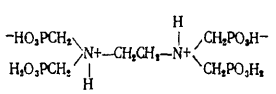
Name of compound	Standard notation	Structural formula	Refs.
Monoaminoalkylphosphonic series			
Nitrilotrimethyl phosphonic acid	H_6ntph		[17]
Cyclohexyliminodimethyl phosphonic acid	H_4cidph		[16]
Ethylaminodimethyl phosphonic acid	H_4eadph		[18]
Diaminoalkylcarboxylic series			
Ethylenediamine-*N,N'*-dipropionic acid dihydrate	$H_2eddp \times 2H_2O$		[4]
Oxamido-*N,N'*-dipropionic acid	H_2oadp		[19]
1,4-Butanediamine-*N,N,N',N'*-tetraacetic acid dihydrate	$H_4dbata \times 2H_2O$		[4]
1,4-Butenediamine-*N,N,N',N'*-tetraacetic acid dihydrate	$H_4dbeta \times 2H_2O$		[4]
2,3-Dihydroxy-1,4-butanediamine-*N,N,N',N'*-tetraacetic acid dihydrate	$H_4dhobta \times 2H_2O$		[20]
Ethylenebis(oxyethylenenitrilo) tetraacetic acid	H_4egta		[21]
Ethylenediamine-*N,N,N',N'*-tetraacetic acid	H_4edta		[22–24]
Ethylenediamine-*N,N'*-disuccinic acid pentahydrate	$H_4edds \cdot 5H_2O$		[25]
trans-1,2-Cyclohexanediamine-*N,N,N',N'*-tetraacetic acid monohydrate	$H_4cdta \cdot H_2O$		[26, 27]
Triaminoalkylcarboxylic series			
Diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid	H_5dtpa		[26, 28]

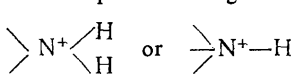
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Name of compound	Standard notation	Structural formula	Refs.
		Diaminoalkylphosphonic series	
Ethylenediamine-*N,N'*-dimethylphosphonic acid dihydrate	H_4eddph×$\times 2H_2O$		[29]
Ethylenediamine-*N,N'*-diisopropylphosphonic acid dihydrate	H_4eddiph×$\times 2H_2O$		[29]
Ethylenediamine-*N,N,N',N'*-tetramethylphosphonic acid monohydrate	H_8edtph		[30]

II. Main structural features of complexones

One of the general problems to be resolved from X-ray diffraction studies on the crystals of compounds that can in principle exist in different forms is the establishment of a correlation between the structure of individual molecules or molecular ions in solution (determined from a combination of physicochemical properties) and their structure in crystals, namely, under conditions of direct and constant contact in time and space between the structural units. This problem relates particularly to the determination of the structural role of separate functional groups of complex molecules under different conditions.

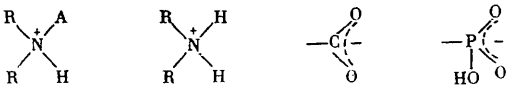
As far as complexones are concerned, there is first of all the question as to the predominant tautomeric form of the molecules. It is known that in aqueous solution complexones, as a rule, have a betaine structure with the positive charge on ammonium centres



(quaternised nitrogen) and the negative charge on one of the acid groups (deprotonated acid group).

Is this type of structure retained in crystals, where the tendency to form a system of N—H...O or O—H...O intermolecular hydrogen bonds can lead to tautomeric rearrangement? What is the relationship between intramolecular and intermolecular hydrogen bonding in a crystal? Would it be possible, despite the individual nature of the crystalline structure of each compound, to establish a general basis for the conformation of complexone molecules and hence to determine experimentally (without calculations) which molecular forms are the most stable? These were the main questions that were raised and resolved in a series of structural studies on complexones carried out at VNII IREA.

An analysis of the results of structural studies on about forty complexones based on mono-, di-, and tri-amines showed that their zwitterion structure is retained in the crystalline state. The molecules contain positively charged ammonium centres (A) or (B) and negatively charged acidic centres (C) or (D) (carboxylate or phosphonate):



(A) (B) (C) (D)

By studying the structure of molecules containing different functional groups, it was possible to establish which of the groups is most susceptible to deprotonation under competitive conditions. Naturally, the group with a higher acidity was deprotonated in all cases. In an IR spectroscopic study of phosphonomethyliminodiacetic acid (H_4phmida) in solution and its deuterium derivative in the solid state[31] it was shown that a zwitterion structure occurs via a proton from the methylphosphonic group rather than a competing acetate group. A study of crystals of H_4phmida and phosphonomethylglycine (H_3phmg) confirmed this result. It was established that in glycinopropionic (H_2gp) and nitrilopropionic diacetic (H_3npda) acids, namely, when acetate and propionate groups are present, the acetate group is deprotonated; in diethanolglycine (Hdeg) and β-hydroxyethyliminodiacetic acid (β-H_2heida) where acetate and β-hydroxyethyl groups are present, the acetate group is deprotonated; in β-hydroxyethyliminodipropionic acid (β-H_2heidp) where β-hydroxyethyl and propionate groups are present, the propionate group is deprotonated; and in iminodisuccinic acid (H_4ids), the more acidic α-carboxyl group rather than the β-carboxyl group is deprotonated. The only exception is nitrilodipropionic acetic acid (H_3ndpa), where a propionate group was found to be deprotonated when an acetate group was present. The explanation of this violation of the general rule is given below. Consequently, the functional groups can be arranged in a series representing a decreasing tendency to undergo deprotonation during competition between acidic groups (for complexones containing different functional groups:

$$CH_2PO_3H_2 > CH_2COOH > CH_2CH_2COOH > CH_2CH_2OH.$$

Thus, in all of the complexones where there are not less than two carboxyl groups per N atom, one of them is always present in the form of a deprotonated carboxylate group (C) (in the absence, of course, of the more active phosphonic group). Similarly in complexes containing not less than two diprotonated phosphonic groups $P(O)(OH)_2$ per N atom, one of them always occurs in the form of a monoprotonated (phosphonate) group (D).

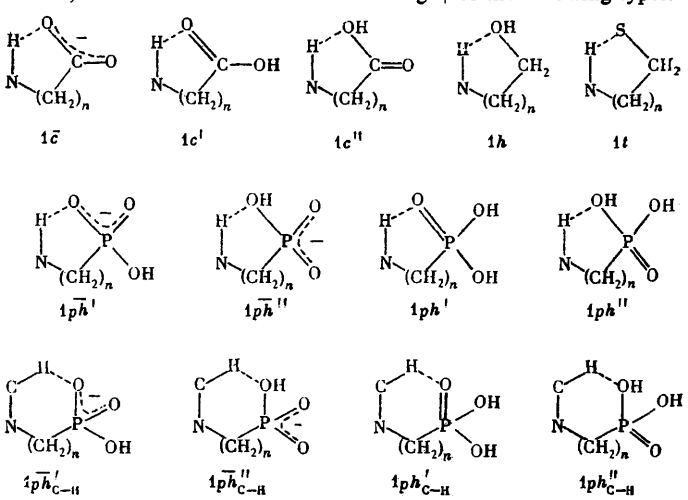
Only in oxamido-*N,N'*-di-3-proprionic acid (H_2oadp) is the betaine structure absent. Nevertheless, even for this compound the formation of intramolecular N—H...O hydrogen bonds is typical (here H is a non-betaine hydrogen atom).

Since the first structurally investigated diaminocarboxylic complexes—H_4edta and H_4edds·$5H_2O$—had a symmetric bis-zwitterion structure with two quaternised N atoms and two deprotonated carboxyl groups, such a structure was also assumed for other diaminocarboxylic complexes for a long time. However, in a study of the structure of H_4cdta an asymmetric betaine structure of the molecule with only one quaternised N atom was found. The presence of another tautomer with a symmetric structure appears to be possible in solution. Incomplete quaternisation of the N atoms (two out of three) was also found in the molecule of the only structurally investigated triaminocarboxylic complexone—H_5dtpa. Incomplete quaternisation of the N atoms does not occur in the structurally investigated diaminophosphonic

complexones, which is probably due to the increased acidity of the phosphonic group compared to the carboxyl group.

The presence of a quaternised nitrogen atom and negatively charged oxygen atoms of acidic groups in complexones increases their tendency to form hydrogen bonds of the type N–H...O. These hydrogen bonds may be both intramolecular (IAHB) and intermolecular (IEHB) and together with other H-bonds they determine the overall molecular conformation, which depends in the long run on the kinetic and thermodynamic advantage for formation of a given system of hydrogen bonding during crystallisation of an acid.

The structural studies carried out indicate that complexone molecules of both monoamino and diamino types always form N–H...O intramolecular hydrogen bonds in addition to intermolecular hydrogen bonds of the type O–H...O and N–H...O, with the N–H group usually participating in IAHB simultaneously with two or three oxygen atoms, i.e., it forms bi- or tri-furcated H-bonds. As an example, the molecule of iminodisuccinic acid (H_4ids) is shown in Fig. 1. Both ammonium hydrogen atoms form bifurcated IAHB, and one of them also participates in IEHB, so that as a whole the H-bond of this N–H group becomes trifurcated. The presence of intramolecular H-rings based on N–H...X hydrogen bonds is one of the most characteristic features of the structure of complexones.[32] The most commonly occurring of them are rings that each contain one nitrogen atom. Amongst the complexes covered in the present review, are to be found mononitrilo-H-rings† of the following types:



† Several different systems of nomenclature for normal H-rings in complexones have already been put forward.[28,33,34] In order to increase their informative capacity and clarity, a new system is proposed in this review: the numeral 1 (as in the studies of Shkol'nikova et al.[28,33]) denotes that only one N atom participates in the formation of an H-ring (we will also consider below rings involving two N atoms, which will be labelled with the numeral 2); *c* denotes carboxylate; *h* is hydroxyethyl; *ph* is phosphonate; *t* is thio; ph_{C-H} is phosphonate with a C–H...O bond. A minus sign above the letters ($\bar{c}$, $\overline{ph}$) is an indication of an ionised group, a single prime against the letter (e.g., *c′*, $\overline{ph}'$) is an indication that a hydrogen bond is formed via the terminal O atom) and a double prime (e.g. *c″*, $\overline{ph}''$) is an indication of hydrogen bonding via the hydroxyl O atom as a hydrogen acceptor. The presence of a $(CH_2)_2$ group instead of CH_2 is recorded using a subscript 2 (e.g. $1\bar{c}_2$, see below).

The first three H-rings ($1\bar{c}$, $1c'$, $1c''$) are nitrilocarboxylic, the fourth ($1h$) is nitrilohydroxyethyl, the fifth ($1t$) (a special case) is analogous to the first, when an O atom is replaced by the heteroatom S. The following four H-rings (second row) are nitriloalkylphosphonic, and the last four are rarely encountered nitrilophosphonic rings with weak C–H...O hydrogen bonding. The rings $1\bar{c}$, $1\overline{ph}'$, $1\overline{ph}''$, $1\overline{ph}'_{C-H}$, and $1\overline{ph}''_{C-H}$ include deprotonated (ionised) acidic groups, the remaining rings involve protonated (formally neutral) groups. They differ from each other according to the nature of the oxygen atom participating in IAHB (while in the rings $1ph'_{C-H}$, and $1ph''_{C-H}$ they differ according to the nature of the proton donor atom). The $(CH_2)_n$ alkyl chain most frequently contains one unit (n = 1), with two units (n = 2) being less frequent.

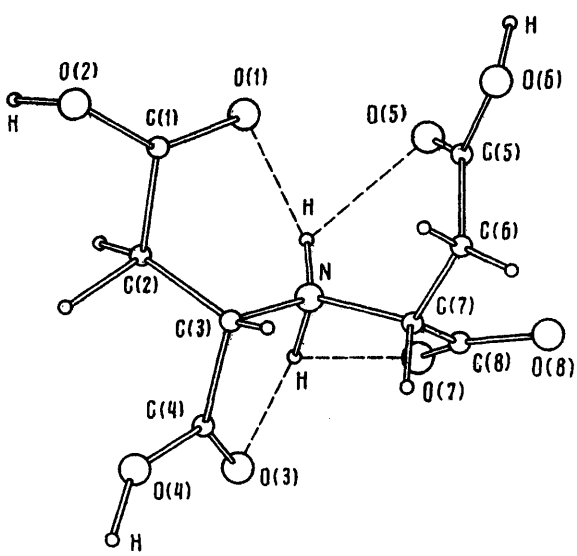


Figure 1. Structure of the iminodisuccinic acid (H_4ids) molecule.

Typical forms of H-ring that include two nitrogen atoms are examined below when the structure of di- and tri-amino complexones is discussed.

The combinations of H-rings in complexone molecules can vary considerably according to the composition of the complexone. Nevertheless, we can consider several quite standard combinations (sets) of H-rings that recur in different compounds. This is especially typical for combinations of five-membered H-rings. As a rule, five-membered H-rings have an envelope conformation, with dihedral angles between the rings lying within the comparatively narrow region of 90–130°. In this respect a clear genetic relationship can be traced between the stereochemistry of mono-, di- and tri-amino complexones.

III. Structure of monoamino complexones

Monoamino complexones can be divided into two groups in accordance with the structural nature of the central ammonium site: complexones with two H atoms on quaternised N (H_2ida class) and complexones with a single hydrogen atom on the betaine unit (H_3nta class).

In the first case, each of the two ammonium protons forms its (or their) independent H-ring, in the second case the H-rings are joined together by a common N–H bond.

The first group, in addition to the three forms of iminodiacetic acid (H_2ida), also includes H_2gp·$2H_2O$, H_3phmg, H_4idph, and H_4ids·H_2O (for labelling of the acids, see Table 1). The remaining 12 monoamino acids studied, including H_3nta itself, belong to the second group.

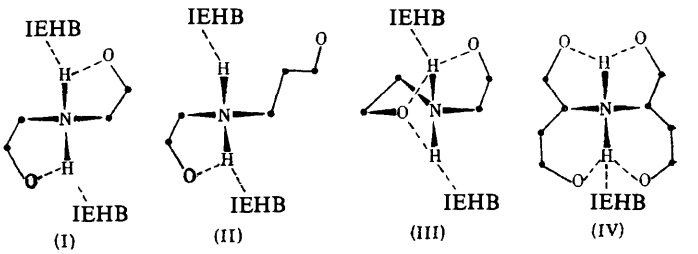
It is clear from the data given in Table 2 that in complexones of the H_2ida class the intramolecular H-bonds are considerably weaker than in complexones of the H_3nta class. This is especially apparent when comparing molecules that are similar in composition. In H_2ida the lengths of the intramolecular H...O bonds in all three modified forms is in the region 2.37–2.63 Å (the exception to this is one H-bond in the A form, where this distance is reduced to 2.16 Å), while in H_3nta the lengths are in the region 2.14–2.26 Å. In the glycinopropionic acid molecule (H_2gp) it is equal to 2.40 Å while in nitrilopropionic diacetic acid (H_3npda) the lengths are 2.13 and 2.27 Å. In H_3phmg the H...O distance to the O atom of the carboxyl group is 2.59 Å whereas in H_4phmida the distances are 2.38 and 2.44 Å and in H_5gdph it is 2.38 Å.‡

It also follows from the data given in Table 2 that the reduced length of the IAHB of the type N–H...O–C on going from H_2ida class complexones to H_3nta class complexones does not depend very much on the nature of the substituents R replacing the second hydrogen atom on nitrogen. Consequently, the cause of the weakening in IAHB in complexones of the first group is the very fact of increasing the number of hydrogen atoms on N. This, firstly, reduces their capacity to interact with O atoms and, secondly, increases the competitive capacity of intermolecular H-bonds, which are less rigidly restricted by the N–H...O angle. As the data of Table 2 also indicate, IEHB is much stronger than IAHB in all cases.

It is somewhat different picture with hydrogen bonding in which oxygen atoms of phosphonic or phosphonate groups participate. In this case the differences in strength of IAHB caused by the different degree of protonation of N atoms disappear, since IAHB of the type N–H...O–P is nearly always much weaker than IAHB of the type N–H...O–C.

a) Complexones of the iminodiacetic acid (H_2ida) class

Amongst the structures of monoaminocarboxylic complexones of the H_2ida class that were studied, four different combinations of IAHB and IEHB occur:



(I) (II) (III) (IV)

The structure of the H_2ida molecule in its two crystalline forms A and C is of a single type; each H forms a single H-ring and one IEHB [scheme (I)]. A similar combination occurs in the two monoaminophosphonic complexones H_3phmg and H_4idph. Replacement of the protonated acetate group by a protonated propionate group on going from H_2ida to H_2gp.$2H_2O$ (and on going from H_3phmg to H_3phma) causes the corresponding IAHB to disappear [scheme (II)]. Studies on other complexones and their cationic forms containing protonated propionate groups showed that H-rings of the type $1c'_2$ which are feasible in H_2gp and H_3phma are only formed when they are joined to other H-rings, and not in all cases (see below), whereas H-rings of the type $1c''_2$ are not formed at all.

In the two crystallographically independent H_2ida molecules with a stable B form, labelled B′ and B″ in Table 2, the formation of uniform sets of hydrogen bonds was detected, as shown in scheme (III). A characteristic of the system of hydrogen bonds here is the joining up of the $1c''$ H-rings along the line of O–C–C–N since the acceptor of IAHB that completes these rings is one and the same hydroxyl O atom of the carboxyl group.

On the whole the H...P distances (IAHB) in this class of aminocarboxylic complexones are in the range 2.37–2.63 Å and the angles at the H atoms are in the range 85–102°. Both these results indicate the weakness of such hydrogen bonds. An exception to this is one of the IAHB in the A form of H_2ida, where the H...O distance is equal to 2.16 Å and the N–H...O angle is 114°. Even less distinct are H-rings involving methylphosphonic groups. Many of them can only be regarded as hypothetical since the H...O distances in them are great as 2.60–2.80 Å, while in H_4cidph even 2.92 Å is attained.

In cyclohexyliminodimethylphosphonic acid (H_4cidph), in addition to a five-membered ring it is also possible to detect a six-membered H-ring (based on a C–H...O bond) of the type $1ph''_{C-H}$, in which the H...O distance is 2.46 Å and the C–H...O angle is 133°. In iminodimethylphosphonic acid a ring of the type $1ph'_{C-H}$ is more representative—the distance is 2.60 Å and angle is 122° (for more details about C–H...O bonds, see below). Naturally, intermolecular hydrogen bonding is much stronger in these compounds than IAHB; the H...O distances are in the range 1.80–2.01 Å (in H_4idph they are 2.12 Å) and the angles at the H atoms increase to 150–180°.

‡ It is assumed that the low accuracy in establishing the position of hydrogen atoms and the variable level of accuracy in structural studies result in a comparison of specific individual distances and angles involving hydrogen atoms not being entirely correct. Therefore, in this case and later in the text we shall examine only general trends that are sufficiently apparent without being dependent on the accuracy of individual figures.

It should be mentioned here that we recognise the actual concept of intramolecular hydrogen bonding to a sufficient extent hypothetically, without limiting the upper limits of the H...O or N...O distances to any specific value (for example, the sum of the van der Waals radii with an additional margin of 0.2 Å). The main criterion for the present authors is the degree of deviation of the C–O (or P–O) bond from the average planarity of the H-ring being formed. We consider that a hydrogen bond actually exists if on the whole the C–O (P–O) bond "faces" towards the ammonium centre of the complexone.

Table 2. Geometric properties of N–H...O hydrogen bonds in the structures of monoaminocarboxylic and monoaminophosphonic complexones.

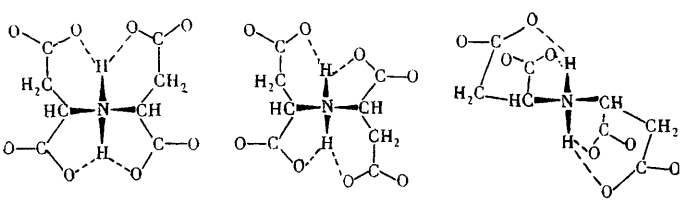
Complexone	Labelling of H-ring or IEHB	Geometry of N–H...O bond				Sets of H-bonds	Angle between rings, deg
		Distance, Å			N–H...O angle, deg		
		N–H	H ..O	N...O			
$H_2ida(A)$	$1\bar{c}$	0.93 (2)	2.16 (3)	2.675 (2)	114 (2)	$1\bar{c}$-IEHB	
	IEHB	0.93 (2)	1.99 (2)	2.674 (2)	149 (2)		
	$1\bar{c}$	0.93 (3)	2.63 (3)	2.733 (2)	86 (2)	$1c'$-IEHB	
	IEHB	0.93 (2)	1.96 (3)	2.807 (2)	151 (2)		
$H_2ida(B')$	$1\bar{c}$	1.10 (6)	2.52 (5)	2.652 (6)	85 (6)	$1\bar{c}$-$1c''$-IEHB	
	$1c''$	1.10 (6)	2.37 (6)	2.657 (6)	93 (5)		
	IEHB	1.10 (6)	1.80 (6)	2.880 (7)	163 (6)		
	$1c''$	0.77 (6)	2.39 (5)	2.657 (6)	102 (6)	$1c''$-IEHB	
	IEHB	0.77 (6)	2.00 (6)	2.750 (5)	161 (5)		
$H_2ida(B'')$	$1\bar{c}$	0.93 (6)	2.60 (6)	2.675 (5)	84 (5)		
	$1c''$	0.93 (6)	2.58 (6)	2.669 (5)	85 (6)	$1\bar{c}$-$1c''$-IEHB	
	IEHB	0.93 (6)	1.90 (6)	2.840 (6)	180 (6)		
	$1c''$	0.86 (6)	2.49 (6)	2.669 (5)	93 (6)	$1c''$-IEHB	
	IEHB	0.86 (6)	2.00 (5)	2.750 (5)	161 (6)		
$H_2ida(C)$	$1\bar{c}$	0.95 (3)	2.45 (4)	2.664 (3)	92 (3)	$1\bar{c}$-IEHB	
	IEHB	0.95 (3)	1.91 (4)	2.812 (3)	157 (3)		
	$1c'$	0.98 (3)	2.44 (4)	2.698 (3)	95 (3)	$1c'$-IEHB	
	IEHB	0.98 (3)	1.81 (3)	2.781 (3)	171 (3)		
$H_2gp \cdot 2H_2O$	$1\bar{c}$	0.80 (6)	2.40 (6)	2.631 (5)	98 (4)	$1\bar{c}$-IEHB	
	IEHB	0.80 (6)	2.01 (6)	2.781 (5)	163 (5)		
	IEHB	1.02 (6)	1.87 (6)	2.813 (6)	153 (5)	IEHB	
$H_4ids \cdot H_2O$	$1\bar{c}$	1.10 (10)	2.02 (10)	2.629 (12)	110 (6)	$1\bar{c}$-$1c'$	108
	$1c'$	1.10 (10)	2.14 (9)	2.623 (11)	102 (6)		
	$1c_2'$	0.89 (8)	2.50 (8)	2.896 (11)	108 (6)		
	$1c_2'$	0.89 (8)	2.39 (8)	2.965 (10)	123 (6)	$1c_2'$-$1c_2'$-IEHB	113
	IEHB	0.89 (8)	2.33 (8)	3.087 (10)	143 (7)		
H_2ids^{2-}	$1\bar{c}$	1.06	2.31	2.69 (1)	99	$1\bar{c}$-$1\bar{c}$	120
in $[Cu(H_2ids)(dipy)_2]$	$1\bar{c}$	1.06	2.06	2.68 (4)	115		
fum.$5H_2O$ (Ref.35)	$1\bar{c}_2$	0.96	1.97	2.70 (1)	131	$1\bar{c}_2$-$1c_2'$	105
	$1c_2'$	0.96	2.29	2.92 (1)	130		
H_3nta	$1\bar{c}$		2.14	2.63		$1\bar{c}$-$1c'$	111
	$1c'$		2.26	2.68			
$Hnta^{2-}$	$1\bar{c}$	0.91	2.26	2.769	115		104
in [Ca(Hnta)].$2H_2OP$ (Ref.36)	$1\bar{c}$	0.91	2.29	2.670	105	$1\bar{c}$-$1\bar{c}$-$1\bar{c}$	108
	$1\bar{c}$	0.91	2.35	2.702	103		98
$Hnta^{2-}$	$1\bar{c}$	1.03	2.10	2.539	103		
in Na[Na(Hnta)] (Ref.37)	$1\bar{c}$	1.03	2.10	2.539	103	$1\bar{c}$-$1\bar{c}$-$1\bar{c}$	
	$1\bar{c}$	1.03	2.10	2.539	103		
H_2nta^-	$1\bar{c}$	0.95	2.35	2.69	100		
in $Ag(H_2nta)$ (Ref.38)	$1\bar{c}$	0.95	2.29	2.67	103	$1\bar{c}$-$1\bar{c}$-$1c'(c'')$	
	$1c'(1c'')$	0.95	2.48	2.78	98		
H_3npda	$1\bar{c}$	1.02 (4)	2.13 (4)	2.680 (4)	111 (3)	$1\bar{c}$-$1c'$-$1c_2'$	103
	$1c'$	1.02 (4)	2.27 (4)	2.736 (4)	106 (3)		93
	$1c_2'$	1.02 (4)	2.50 (4)	3.097 (4)	117 (3)		147
H_3ndpa	$1\bar{c}_2$	0.85 (7)	2.11 (7)	2.788 (7)	137 (6)	$1\bar{c}_2$-$1c'$	118
	$1c'$	0.85 (7)	2.23 (7)	2.658 (7)	111 (6)		
H_3ntp	$1\bar{c}_2$	1.02 (4)	2.11 (4)	2.803 (4)	123 (3)	$1\bar{c}_2$-$1c_2'$	109
	$1c_2'$	1.02 (4)	2.31 (4)	3.003 (4)	124 (3)		
Hndpma	$1\bar{c}$	0.92 (2)	2.13 (2)	2.669 (2)	116 (2)		90
	$1c_2'$	0.92 (2)	2.40 (2)	2.937 (2)	120 (2)	$1\bar{c}$-$1c_2'$-$1c_2'$	149
	$1c_2'$	0.92 (2)	2.37 (2)	3.001 (2)	127 (2)		114
Hdeg	$1\bar{c}$	0.85	2.19	2.670	116		111
	$1h$	0.85	2.31	2.743	112	$1\bar{c}$-$1h$-$1h$	119
	$1h$	0.85	2.31	2.738	111		115

Table 2 (cont'd).

Complexone	Labelling of H-ring or IEHB	Geometry of N–H...O bond				Sets of H-bonds	Angle between rings, deg
		Distance, Å			N–H...O angle, deg		
		N–H	H ..O	N...O			
β-H_2heida	$1\bar{c}$	0.84 (3)	2.27 (3)	2.654 (3)	100 (2)	$1c$-$1c''$-$1h$	91
	$1c''$	0.84 (3)	2.40 (3)	2.679 (3)	101 (2)		116
	$1h$	0.84 (3)	2.21 (2)	2.688 (4)	116 (2)		108
β-H_2heidp	$1\bar{c}_2$	0.93 (2)	2.12 (2)	2.826 (2)	132 (1)		120
β-H_2heidp	$1c_2'$	0.93 (2)	2.48 (2)	3.054 (2)	121 (1)	$1\bar{c}_2$-$1c_2'$-$1h$	107
	$1h$	0.93 (2)	2.61 (1)	2.998 (2)	105 (1)		116
H_3meata·H_2O	$1\bar{c}$	0.89 (3)	2.26 (3)	2.663 (3)	107 (3)	$1\bar{c}$-$1c'$-$1t$	111
	$1c'$	0.89 (3)	2.26 (3)	2.678 (3)	108 (3)		
	$1t$	0.89 (3)	2.61 (3)	3.139 (3)	119 (3)		
H_2mida	$1\bar{c}$	0.98 (2)	2.15 (2)	2.651 (2)	110 (2)		
	$1c'$	0.98 (2)	2.46 (2)	2.739 (2)	97 (1)	$1c$-$1c'$-IEHB	90
	IEHB	0.98 (2)	2.06 (2)	2.856 (2)	138 (2)		
H_3phmg	$1c'$	0.94 (2)	2.59 (2)	2.761 (1)	90 (1)	$1c'$-IEHB	
	IEHB	0.94 (2)	1.95 (2)	2.818 (1)	158 (2)		
	$1\overline{ph'}$	0.86 (2)	2.77 (2)	2.998 (1)	97 (2)	$1\overline{ph'}$-IEHB	
	IEHB	0.86 (2)	1.93 (2)	2.733 (1)	154 (2)		
H_3phmg	$1c'$	0.86 (4)	2.46 (3)	2.665 (3)	93 (3)	$1c'$	
in H_3phmg.½HCl (Ref.39)	IEHB	1.00 (4)	1.99 (3)	2.932 (3)	154 (3)	IEHB	
H_3phma	IEHB	0.93 (4)	1.99 (4)	2.932 (3)	173 (4)	IEHB-IEHB	
	IEHB	0.93 (4)	1.96 (4)	2.806 (3)	148 (4)		
H_4idph	$1ph''$	0.86 (5)	2.53 (5)	2.853 (4)	103 (3)	$1ph''$-IEHB	
	IEHB	0.86 (5)	2.12 (5)	2.884 (4)	149 (4)		
	$1\overline{ph'}$	0.84 (5)	2.77 (5)	2.968 (4)	95 (4)		
	IEHB	0.84 (5)	1.89 (3)	2.708 (4)	165 (5)	$1\overline{ph'}$-IEHB	
H_4phmida	$1c'$	0.85 (6)	2.38 (6)	2.737 (5)	106 (5)	$1c'$-$1c''$-IEHB	
	$1c''$	0.85 (6)	2.44 (6)	2.709 (5)	100 (5)		
	IEHB	0.85 (6)	1.99 (6)	2.763 (4)	151 (6)		
H_5gdph·$2H_2O$	$1c'$	1.09 (7)	2.38 (6)	2.732 (4)	96 (4)	$1c'$-$1\overline{ph'}$-IEHB	
	$1\overline{ph'}$	1.09 (7)	2.50 (6)	2.885 (4)	101 (4)		
	IEHB	1.09 (7)	1.84 (7)	2.892 (3)	159 (5)		
H_6nlph	$1\overline{ph'}$	0.94	2.66	3.160	114	$1\overline{ph'}$-$1ph'$-IEHB	
	$1ph'$	0.94	2.48	2.858	104		
	IEHB	0.94	2.02	2.842	144		
H_4cidph	$1\overline{ph'}$	0.79 (3)	2.80 (3)	3.077 (3)	103 (2)	$1\overline{ph'}$-$1ph'$-IEHB	
	$1ph'$	0.79 (3)	2.92 (3)	3.118 (2)	97 (2)		
	IEHB	0.79 (3)	1.91 (3)	2.697 (3)	171 (3)		
H_4eadph	$1ph''$	0.81 (8)	2.70 (9)	3.140 (4)	116 (8)	$1ph''$-IEHB	
	IEHB	0.81 (8)	2.07 (9)	2.810 (4)	152 (8)		

It is the weakness of IAHB (both relative and absolute) that leads to the stereochemical diversity of molecules of the H_2ida class. The molecules have a conformational flexibility and they readily change their conformation under the influence of IEHB. The existence of different crystalline forms of H_2ida is probably also a consequence of this.

Iminodisuccinic acid (H_4ids) can also formally be assigned to the H_2ida class [scheme (IV)]. The IAHB in it proved to be considerably stronger than in the remaining compounds of this class. The H_4ids molecule contains two succinate groups, which may be regarded as propionate groups with one of the H atoms replaced by a carboxyl group. It was established from X-ray diffraction studies that one of the α-carboxyl groups is deprotonated in accordance with its higher acidity compared to the β-group. In principle three ways of forming H-rings in H_4ids are possible, depending on the different combinations of IAHB involving the α- and β-carboxyl groups:



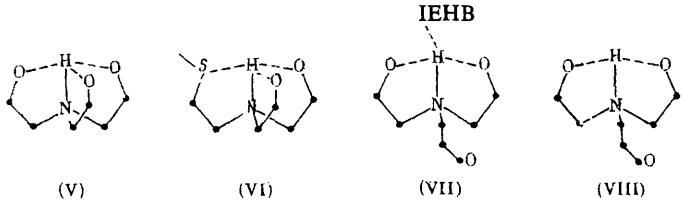
(A) (B) (C)

On crystallisation from solution, crystals in the form of (A) (Fig. 1) are isolated. The H_4ids molecule has a compact and probably the most favourable configuration energetically irrespective of intermolecular interactions, confirmation of which is its retention

in the structure of the heteroligand complex $[Cu(H_2ids)(bipy)_2]\cdot 0.5fum\cdot 5H_2O$, where fum = fumaric acid. The H_2ids^{2-} anion retains its betaine structure with monodentate coordination to the Cu atom and has a system of IAHB similar to that of the neutral molecule (see Table 2). One H atom completes two five-membered rings and the other is included in two six-membered rings, the strength of the O...H bonds within each pair of rings being different.

b) Complexones of the nitrilotriacetic acid (H_3nta) class

The single ammonium (betaine) H atom on the N atom in complexones of the H_3nta class is highly active in forming hydrogen bonds, joining up at least two and sometimes three functional groups. Moreover, it participates in the formation of an H-bond with a heteroatom X if the latter is present in the molecule. In complexones of this class it is also possible for four different sets of H-rings to occur:



(V) (VI) (VII) (VIII)

Scheme (V) depicts the structure of $Hnta^{2-}$, H_2nta^-, H_3npda, Hdeg, β-H_2heida, β-H_2heidp, and Hndpma; scheme (VI) depicts the structure of $H_3meata.H_2O$; scheme (VII) shows the structure of H_2mida, $H_4phmida$, H_4cidph; and the structure of H_3nta, H_3ndpa, H_3ntp, and H_5gdph is shown in scheme (VIII).

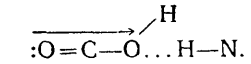
The largest number of examples is included in the first group, where the trifurcated intramolecular N—H...O bond uses the oxygen atoms of all three functional groups as acceptors. Complexones which are characterised by the type of bonding in (VI), where one of the N—H...O bonds is replaced by an N—H...S, have a similar structure (concerning the similarity of the structure of this complexone and the diamino H_4cdta, see below). This type of structure can be called "closed".

Considerably different are the bonding variants (VII) and (VIII), in which one of the functional branches has a transoid rather than the usual twisted conformation relative to the N—H bond, which leads to the disappearance of one of the IAHB ("semi-closed" structure).

In complexones with a closed structure are to be found combinations of acetate groups and propionate, β-hydroxyethyl, and β-propionamide groups, or propionate groups combined with β-hydroxyethyl groups (in β-H_2heidp). It is true that H_3nta itself has a semi-closed structure (one of the two protonated acetate groups does not form an H-ring). However, the anionic forms of this acid (not only nta^{3-} and $Hnta^{2-}$ but also H_2nta^-) have a closed structure. The same applies to H_2nta^- in $Ag(H_2nta)$ and $Hnta^{2-}$ in $Ca(Hnta)\cdot 2H_2O$ and $Na[NaHnta]$.

The β-H_2heida molecule has one interesting feature. Instead of the usual $1c'$ glycine H-ring it contains an unusual $1c''$ isoglycine ring with a set of three H-rings ($1\bar{c}$-$1c''$-$1h$) being formed. It would seem that the reason for the inversion of the —COOH group might be the participation of the carboxyl O atom in an energetically more favourable intermolecular O...H—O or O...H—N interaction. However, despite the favourable configuration of the C=O group for this type of interaction, the carboxyl oxygen atom remains completely inert in relation to formation of IEHB of the type O...H—O or O...H—N but, on the other hand, participates in relatively weak IEHB of the type O...H—C.

It is known that IEHB of the type O...H—C is typical of amino acids, peptides, and other bioorganic compounds in which the N atom has an activating effect on the H atom of the neighbouring CH-, CH_2- or CH_3-group.[40] In the case of β-H_2heida the transition to a C—H...O bond, moreover, is encouraged by the weakening of the nucleophilic properties of the carbonyl O atom as a result of the withdrawal of electron density from it along the chain



A complexone which stands somewhat apart from amongst closed complexones of the H_3nta class is β-H_2heidp, in which a set of three H-rings ($1\bar{c}_2$-$1c'_2$-$1h$) is formed from two propionate groups and one hydroxyethyl group. The presence of two six-membered H-rings results in a significant weakening of the H-bond in the $1h$ ring containing the hydroxyethyl group compared to the analogous H-bonds in Hdeg and β-H_2heida, where this H-ring is combined with two five-membered rings.

The remaining complexes of the H_3nta class that were studied have a semi-closed structure. This applies not only to H_3nta itself but also to its analogue H_3ntp. Replacement of the acetate groups in H_3nta by propionate groups does not in principle change anything. Only instead of a combination of two five-membered H-rings ($1\bar{c}$-$1c'$) there is a combination of two analogous six-membered rings ($1\bar{c}_2$-$1c'_2$) (Fig. 2*a*). It is true that the conformation of the third functional group (—CH_2COOH and —CH_2CH_2COOH respectively), which does not participate in IAHB, is considerably different in the structures of the two acids; the H—N—C—C torsion angles in them are 174 and 48° respectively. But although in this first "bend" because of the small size of the torsion angle this branch in H_3ntp is capable of forming an H-ring, its second "bend", having a planar *trans* structure, turns the O atoms away from the betaine proton. The conformation of the group not participating in the formation of an H-bond is apparently determined by the packing requirements of the crystalline structure as a whole.

A similar structure occurs for nitrilodipropionic acetic acid (H_3ndpa) (Fig. 2*b*), but not for nitrilopropionic diacetic acid (H_3npda). In the latter all three H-rings are formed (Fig. 2*c*). While the semi-closed structure of H_3nta is considered to be an unusual coincidence, it may be assumed that the bifurcate nature of H-bonding in H_3ndpa and H_3ntp arises from the difficulty of forming at the same time two (even more so three) six-membered alanine H-rings because of the steric hindrance that occurs (the weakening of the H-bond involving the hydroxyethyl group in β-Heidp, as mentioned above, is an indication of this).

On the whole the observed variety of combinations of H-rings in the crystals of acids of the H_3nta class with a similar composition, and in particular in the series H_3nta—H_3ntp, is an indication of the strong dependence of the molecular conformation on apparently insignificant changes in the nature of the functional groups in the complexone. However, the possibility cannot be excluded that in solution there are different conformers, whose molecules contain a different number of H-rings. Nevertheless, it should be emphasised that in all of the complexones of this class, regardless of the nature of IAHB (bi- or tri-furcated), uniform sets of H-rings are formed. There is no doubt that the effect of intermolecular interactions is exhibited here to a very much smaller degree than in

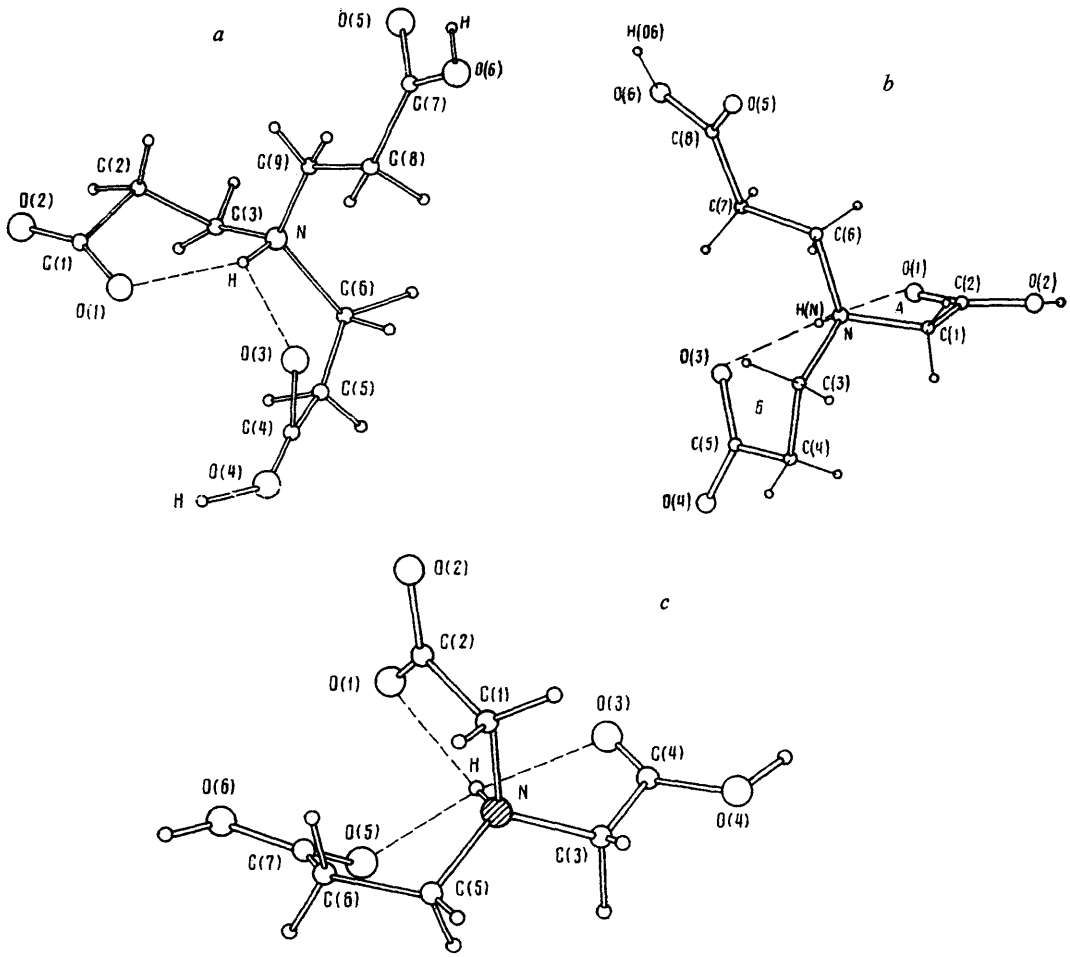


Figure 2. Structure of nitrilotripropionic acid (H_3ntp) (*a*), nitrilodipropionic acetic acid (H_3ndpa) (*b*), and nitrilopropionic diacetic acid (H_3npda) molecules (*c*).

monoaminocarboxylic complexones of the H_2ida class or in aminophosphonic complexones of both classes.

The structural data on "closed" and "semi-closed" compounds of the H_3nta class is sufficiently extensive to permit comparison between the geometric characteristics of H-rings of different types.

In rings of the type $1\bar{c}$ the H...O distances are 2.13–2.27 Å and the angles at the H atoms are 100–116°, while in rings of the type 1*c*′ these values are 2.26–2.46 Å and 97–111° respectively. These results indicate a weakening of IAHB on going from glycinate to glycine H-rings. The change from compounds with a "semi-closed" structure to a "closed" structure on deprotonation of H_3nta to H_2nta^- and $Hnta^{2-}$, for example, may be confirmation of this.

There are considerably less structural data on 1*h* and particularly 1*c*″ rings. In the 1*h* rings present in Hdeg and β-H_2heida, the H...O distances are in the range 2.21–2.31 Å and the angles at the H atom are 111–116°. In the structure of β-H_2heidp, as was indicated above, there is a pronounced weakening of the H...O bond forming the 1*h* ring (H...O distance 2.61 Å), namely, replacement of acetate groups by propionate groups causes this distance to increase by ~0.4 Å. Further replacement of a hydroxyethyl group by a propionate group in H_3ntp leads to complete ring-opening of one of the H-rings. These changes constitute a clear display of the mutual effect of the H-rings and are probably caused by steric factors.

1*c*″ H-rings were only detected in β-H_2heida and H_4phmida; the H...O distances in them are equal to 2.40 and 2.44 Å and the angles at the H atoms are 101 and 100°. Because of the lack of data, it may be concluded only provisionally that the 1*c*″ isoglycine rings have the lowest strength while the $1\bar{c}'$ glycine and 1*h* nitrilohydroxyethyl rings have approximately the same strength but lower than for $1\bar{c}$ glycinate rings.

The intermediate position of the 1*h* ring is supported by a comparison of the geometry of IAHB in Hdeg and β-H_2heida. In the first of these the H-bond involving the $1\bar{c}$ glycinate group is considerably stronger than that involving the 1*h* hydroxyethyl group, in the second the H-bond involving the hydroxyethyl group is stronger than that involving the 1*c*″ isoglycine group. The H...O distances in $1\bar{c}_2$ alanine rings are almost constant (~2.11 Å) and are virtually no different from the lower limit of the distances in $1\bar{c}$ rings. On the other hand, in $1c'_2$ alanine rings, as in 1*c*′ rings, the

H...O distances vary over a wide range and are also considerably longer than those in $1\bar{c}$ rings (2.31–2.50 Å).

The transition from five-membered to six-membered rings gives rise to considerably greater changes in the angles at the H atoms. They increase substantially (by more than 20°)—123–137° in the case of $1\bar{c}_2$ and 117–127° for $1c'_2$.

IAHB is least strong in aminophosphonic complexones. This applies primarily to the phosphonate or phosphonic groups themselves. In many cases they do not participate at all in the formation of H-rings (such as H_4phmida, H_6ntph, H_5gdph, H_4eadph, H_3phmg, and in the structure of H_3phmg·½HCl). Sometimes the formation of H-rings can only be hypothetically assumed, since the H...O distances in them increase to 2.48–2.92 Å. The other types of H-rings in these compounds also prove to be weakened, in particular for $1c'$ (in H_3phmg, H_4phmida, H_5gdph the H...O distances are 2.38–2.59 Å and the angles at the H atom are 90–106°), while a $1h_2$ ring is not formed at all in H_3phma (only intermolecular H-bonds occur in the structure). It would appear that in the case of monoaminophosphonic complexones it is only possible to indicate that there is a tendency to form H-rings, which occurs only when the molecular packing conditions are favourable.

These same groups, $-CH_2PO_3H^-$ and $CH_2PO_3H_2$, are possibly dependent on a purely conformational factor. Non-bonded interactions between the substituents in the two tetrahedral groups—phosphonic and methylene—make the most eclipsed conformation necessary for the approach of one of the atoms of the phosphonate group to the ammonium atom less favourable.

The groups described may be arranged in the following series of decreasing H-acceptor activity:

$$COO^- > COOH_{=O} > CH_2CH_2OH > COOH_{OH} > PO_3H^-,\ PO_3H_2$$

IV. Structure of diamino and triamino complexones

The list of structurally investigated diamino complexones known to the present authors includes eight diaminocarboxylic acids, four of their cationic and three of their anionic forms, three diaminophosphonic complexones and the cationic form of one of these (Table 1). The structure of a single triaminocarboxylic complexone is also known.

By analogy with monoamino complexones, diamino complexones can also be divided into two classes: those with ammonium centres each containing two hydrogen atoms [the ethylenediamine-*N*,*N'*-diacetic acid (H_2edda) class] and those with ammonium centres each containing one betaine hydrogen atom [the ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (H_4edta) class].

Depending on the nature of the intramolecular H-rings formed, diamino complexones of both classes can be subdivided into three groups—open, semi-open, and closed. Compounds that do not form IAHB belong to the first group. In fact, this type of structure only occurs for the cationic forms of two complexones with propionate substituents—H_4eddp^{2+} and H_6edtp^{2+} as their hydrochlorides.

The second group includes compounds whose IAHB only join atoms that belong to their "own" half of the diamino complexone. H-rings characteristic of monoamino complexones are formed, and also as a rule in similar combinations, so such complexones can be called "quasi-monoamino".

The third group is made up by complexones that contain "crossed" IAHB between the atoms of the different halves of the molecule in addition to the IAHB of each monoamino moiety.

It is not difficult to realise that the formation of closed diamino complexones requires a twisted structure of the central (usually ethylenediamino) section. Complexones with a semi-open and open structure always have an unfolded transoid structure of the central section, which may be both the cause and the effect of the quasi-monoamino nature of their system of IAHB. The H_4eddp^{2+} cation, which has an open structure, and the H_2eddp molecule with a semi-open structure, are shown in Fig. 3*a* and 3*b* as examples.

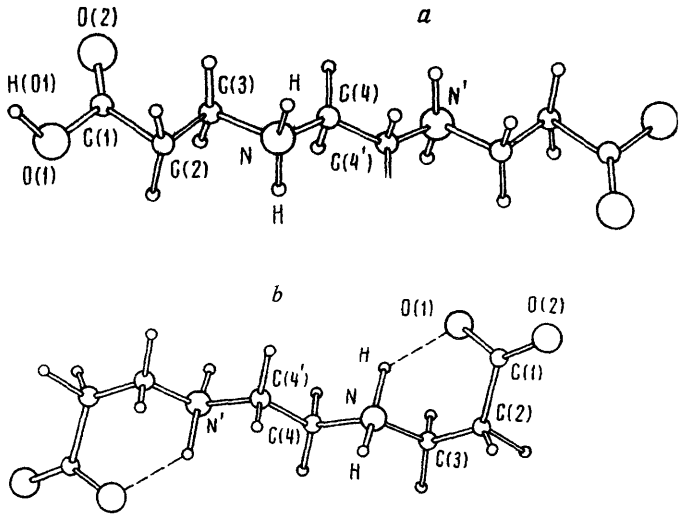


Figure 3. Structure of the H_4eddp^{2+} cation (*a*) and ethylenediamine-*N*,*N'*-dipropionic acid (H_2eddp) molecule (*b*).

In Table 3 all of the diamino complexones (and the triamino H_5dtpa) of both classes are assigned to their respective groups. It follows from Table 3 that almost all of the complexones from the H_2edda class have an open or semi-open structure. The presence of two H atoms on each ammonium centre is likely to lead to the degree of weakening of IAHB of the type N–H...O at which the strained folded structure becomes unstable. The only exception is $H_4edds·5H_2O$, which is probably related to the specific nature of the succinate groups.

Amongst those compounds that belong to the H_4edta class, all three structural variants have been found—open (in the H_6edtp^{2+} cation), semi-open (in five neutral molecules, two anions, and one cation), and closed (in five neutral molecules, one anion, and one cation).

As expected, a semi-open structure occurs in complexones with an elongated or complex hydrocarbon chain in the central section, as in H_4dbata, H_4dbeta, H_4dhobta, H_2oadp, and H_4egta (see Table 1 for structural formula), which hinders the formation of crossed hydrogen bonds. The molecules of H_2oadp§ and H_4dhobta are

§ The structure of the H_2oadp complexone is unique. This complexone is intermediate between semi-open and closed types. Its central section contains two carbonyl O atoms, so that it can form two intersecting five-membered H-rings without changing to a twisted conformation. Similar rings are also retained in the $oadp^{2-}$ anion, which is coordinated on two sides with Cu atoms in $[Cu(oadp)(bipy)(H_2O)_2]·H_2O$ (Fig. 4*b*).

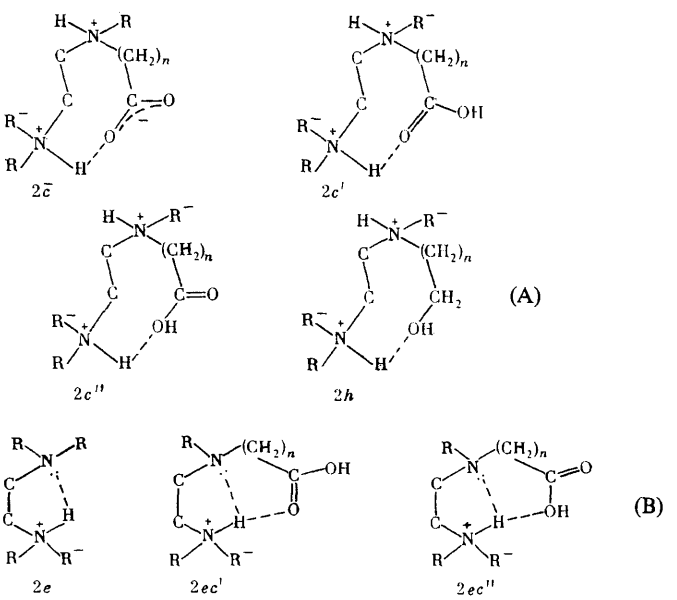
Table 3. Division of structurally investigated diamino and triamino complexones and their cationic and anionic forms into classes (H_2edda and H_4edta) and groups (different types of structure).

Group	H_2 edda class	H_4 edta class
Open structure	$[H_4eddp]^{2+}$ в $[H_2eddp]\cdot 2HCl$	$[H_6edtp]^{2+}$ в $[H_4edtp]\cdot 2HCl$
Semi-open structure (unfolded conformation of the central section)	$H_2eddp\cdot 2H_2O$ $H_4eddph\cdot 2H_2O$ $H_4eddiph\cdot 2H_2O$ $[H_6eddiph]^{2+}$ в $[H_4eddiph]\cdot 2HCl\cdot 2H_2O$ H_2oadp $oadp^{2-}$ в $[Cu(oadp)bipy(H_2O)_2]\cdot H_2O$	$[H_6edta]^{2+}$ в $[H_4edta]\cdot 2HCl\cdot 3H_2O$ $[H_2edta]^{2-}$ в $[Mg(H_2O)_6](H_2edta)$ $[H_2edta]^{2-}$ в $[Rb_2(H_2edta)]\cdot 2H_2O$ $H_4dbata\cdot 2H_2O$ $H_4dbeta\cdot 2H_2O$ $H_4dhobta\cdot 2H_2O$ $[H_5edta]^{+}$ в $[H_4edta]HBr\cdot H_2O$
Closed structure (twisted conformation of the central section)	$H_4edds\cdot 5H_2O$	H_4edta $[H_2edta]^{2-}$ в $K_2(H_2edta)\cdot 2H_2O$ $H_4cdta\cdot H_2O$ $[H_6cdta]^{2+}$ в $[H_6cdta][PdCl_4]$ H_5dtpa $H_8edtph\cdot H_2O$

depicted in Fig. 4*a* and 4*c* as examples. More curious and less easy to understand is the fact that anionic forms of the reference complexes H_2edta^{2-} in two compounds (Rb and Mg salts), in the same way as the cationic form H_5edta^{+} in hydrobromide, have an unfolded structure, while the same H_2edta^{2-} anion in the potassium salt and the acid itself (H_4edta) have a twisted conformation. This disparity evidently indicates that both forms are approximately equivalent in terms of energy and they are selected according to the specific composition of the compound as a whole. In particular, the change to a strongly acid medium, which creates the conditions for the formation of H_5edta^{+} from H_4edta, results in cleavage of the crossed N—H...O bonds, and hence leads to the conformation of the central section changing from twisted to transoid (Fig. 5*a* and 5*b*).

Finally, it is worth noting that neither the absence nor the presence of crossed IAHB are necessarily an indication of "symmetry" of the composition and conformation of the substituents of the two halves of the molecule. Symmetry in protonation of the carboxylate groups is absent, in particular in the semi-open H_4dhobta (Fig. 4*b*) and in the protonation of N atoms in H_4cdta (but not H_6cdta^{2+}) and H_5dtpa (Figs. 6 and 7). Finally, in the phosphonic complexone H_8edtph (Fig. 8), while there is complete "symmetry" of composition (see Table 3), symmetry is absent in the formation of IAHB. The structural features of these complexones will be examined below in greater detail.

In the molecules and ions with a semi-open structure, only those H-rings which are characteristic of monoamino complexones are possible. In complexones of a closed structure with crossed H-bonds, additional H-rings are formed, containing two nitrogen atoms:



The first group (A) comprises eight-membered rings (when $n = 1$) with N—H...O bonds; these are $2\bar{c}$, $2c'$, and $2c''$ H-rings based on a carboxylate substituent and a $2h$ H-ring based on a hydroxyethyl

substituent.¶ The second group (B) is made up by five-membered H-rings (when $n = 1$) with N–H...N bonds that occur when one of the two nitrogen atoms is quaternised; these are 2*e* (in a pure form), 2*ec'* and 2*ec''* (with additional expansion to eight-membered cyclic analogues of 2*c'* and 2*c''* rings). Such rings occur in the diamino H_4cdta and the triamino H_5dtpa (see structural formulae in Table 1 and Figs. 6 and 7). We should point out that the five-membered 2*e* ring may be regarded as an analogue of a 1*t* ring and hence a diamino complexone may formally be regarded as a monoamino complexone (and triamino like diamino) with an N heteroatom (carrying an unshared electron pair) as one of the substituents.

Let us pause to consider asymmetric complexones in somewhat greater detail. It is clear from Fig. 4*c* that the asymmetry of H_4dhobta arises not only because both carboxyl groups bound to one N atom are deprotonated while both of those bound to the other N* nitrogen atom are protonated. The difference also occurs because the H(N) atom takes part in the formation of a trifurcated bond with the two ionised atoms O(1) and O(3) and with the O(5) atom of the hydroxyl group in the neutral residue, while the H(N)* only participates in a bifurcated bond with the carbonyl atoms O(1)* and O(3)*. This results from the specific manner of unfolding of the successive units of the chain in the central section, leading to a convergence of the O(5) and H(N) atoms but not the O(5)* and H(N)* atoms.

The structure of the H_4cdta molecule, in which only one N(1) atom is quaternised, is depicted in Fig. 6. Its H(N1) proton participates accordingly in the formation of a trifurcated bond, forming a five-membered 2*e* ethylenediamine (*E*) H-ring and five-membered $1\bar{c}$ glycinate (*A*) and 1*c'* glycine (*B*) rings.

The structure of the triamino complexone H_5dtpa is shown in Fig. 7. Here also not all but only two of the three nitrogen atoms—the central N(1) atom and one of the lateral N(2) atoms—are quaternised, although the lateral nitrogen atoms are known to have a higher basicity than the central atom. In essence, the molecule may be regarded as a diamino complexone with a bis-zwitterion structure [the N(1) and N(2) atoms] and an analogue of H_4edta with replacement of one of the acetate groups by an ethyleneaminoacetate group. The N(2) atom, in the same way as in H_4edta, belongs simultaneously to three conjugated H-rings involving acetate groups (rings *A*, *B*, and *C* in Fig. 7), one of which (*C*) is crossed. Replacement of one of the acetate groups on the N(3) atom by an ethyleneaminoacetate group permits the H(N1) atom to form only two rings—an ethyleneamino ring (*E*), the same as in H_4cdta, and an eight-membered ring involving an acetate group (*D*), namely the combination labelled above as 2*ec'*. The geometric properties of the N–H...N bond in H_5dtpa and H_4cdta are very similar (Table 4). Thus, both the molecular geometry and the system of IAHB in H_5dtpa combine typical features of H_4edta and H_4cdta. The triaminocarboxylic complexone is made up of standard sets of H-rings that are typical of monoamino- and diamino-carboxylic complexones.

Perhaps the most individual structure is that of the methylphosphonic diamino complexone H_8edtph (Fig. 8) (for structural formula, see Table 1).

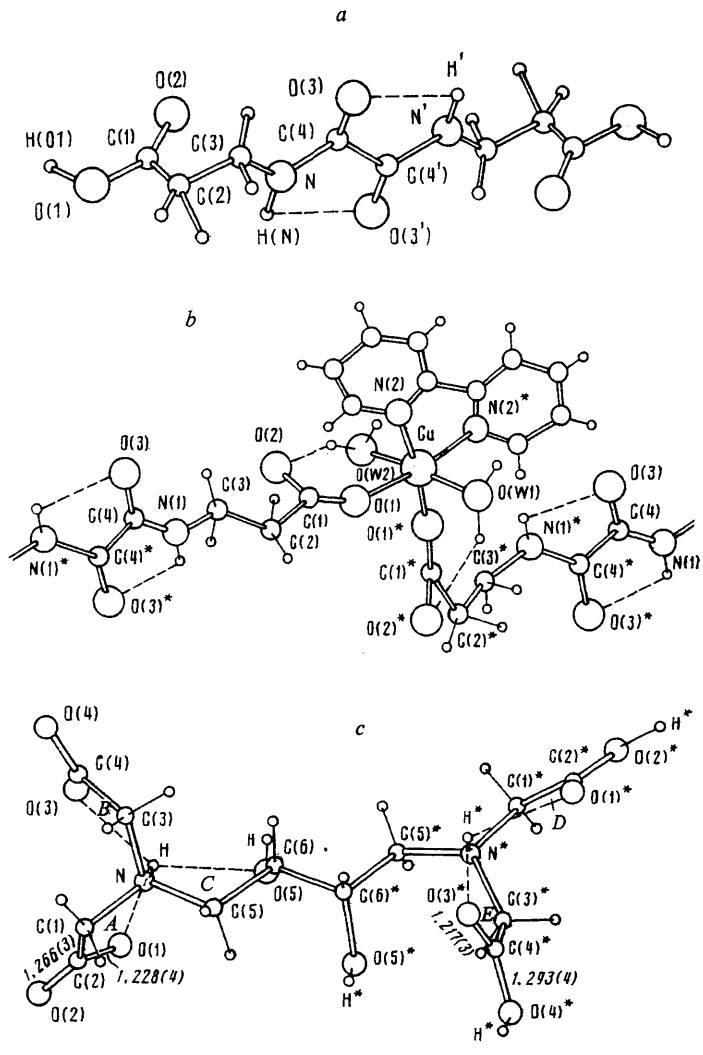


Figure 4. Structure of the oxamido-*N*,*N'*-dipropionic acid (H_2oadp) molecule (*a*), a section of the polymeric chain structure of $[Cu(oadp)(bipy)H_2O)_2]\cdot H_2O$ containing $oadp^{2-}$ anions (*b*), and the 2,3-hydroxy-1,4-butanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid molecule (*c*). Primes are used to denote atoms that are related by symmetry elements and asterisks are used to denote crystallographically independent atoms in the second half of the molecule.

At first glance it resembles the structure of the H_4edta molecule. It has the same twisted conformation of the central ethylenediamino residue (with a dihedral angle of 86° instead of 67°), there are H-rings that include only their "own" phosphonate and also "crossed" rings that involve a "foreign" phosphonate group. In fact, however, there is only one nitrilomethylphosphonate H-ring ($1\overline{ph}$) (ring *A* in Fig. 8); the remaining three six-membered rings—$1\overline{ph}''_{C-H}$ and $1ph'_{C-H}$ (crossed) and $1ph''_{C-H}$ (terminal) (*B*, *C*, and *D*)—are formed by C–H...O bonds rather than N–H...O.

¶ Variants based on phosphonate or phosphonic groups have not been given since molecules with such types of H-ring have so far not been detected.

The specific nature of methylphosphonic complexones is manifested in this (as mentioned above in connection with similar IAHB in monoamino complexones). It is natural that the hydrogen bonds in these H-rings are some of the weakest.

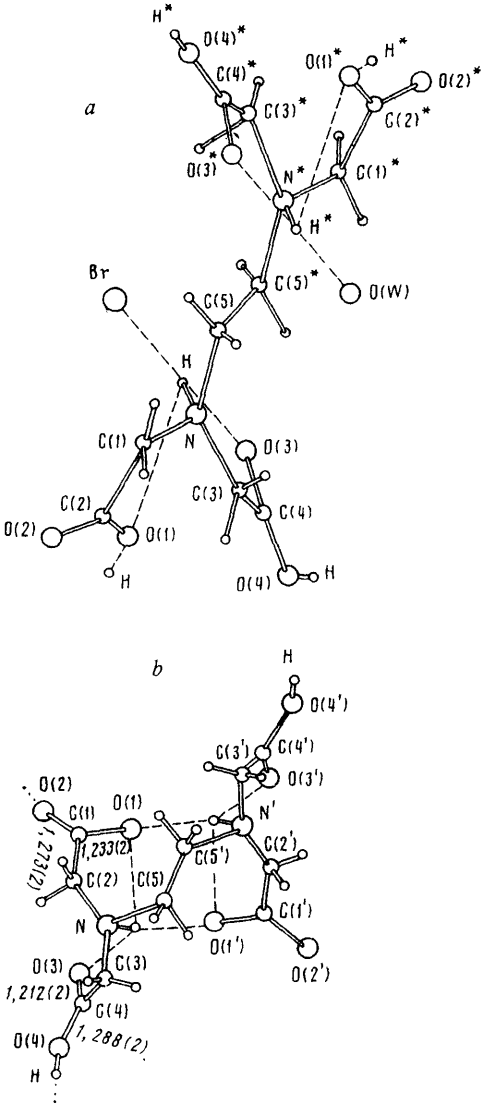
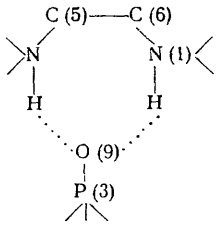


Figure 5. Structure of the H_5edta^+ cation (*a*) and ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (H_4edta) molecule (*b*).

N^+-H groups of the central section of the molecule



so that a seven-membered H,H-ring is formed.

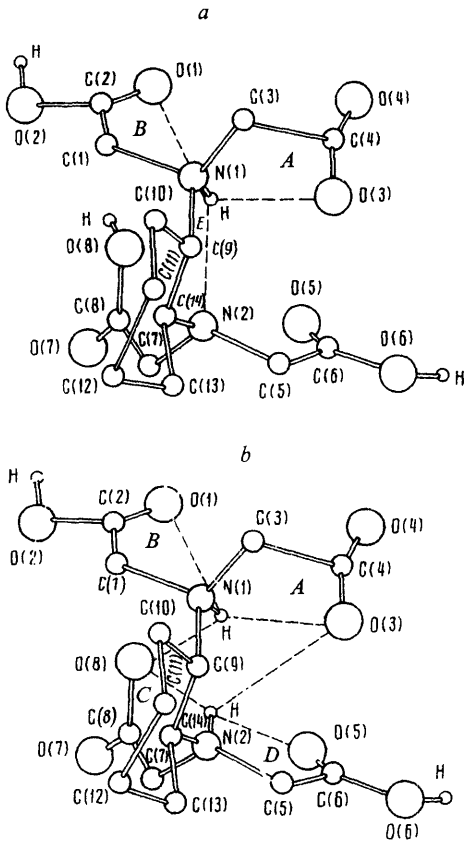


Figure 6. Structure of the *trans*-1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid molecule (*a*) and its hypothetical tautomeric form (*b*).

In H_8edtph there is perhaps the clearest exhibition of the tendency of methylphosphonate complexones to form intermolecular N−H...O hydrogen bonds involving the oxygen of a phosphonic or phosphonate group rather than intramolecular hydrogen bonds. An unusual feature of the crystalline structure of this compound is also that the O(9) atom of the phosphonate group of the neighbouring complexone forms an IEHB simultaneously with two

In the majority of the asymmetric complexones described there are short intermolecular hydrogen bonds of the type O...H...O, where the potential lability of the proton makes the description of the sets of H-rings in them not completely unequivocal (it opens up the possibility of a $1\bar{c}$ ring involving a COO^- group being replaced by a $1c'$ or $1c''$ ring involving a COOH group and vice versa). This question is considered in greater detail in the next section.

The geometric properties of hydrogen bonding (IAHB and IEHB) in the diamino and triamino complexones studied are given in Table 4. The labelling of the "sets"—the combinations of conjugated H-rings—is also given here.

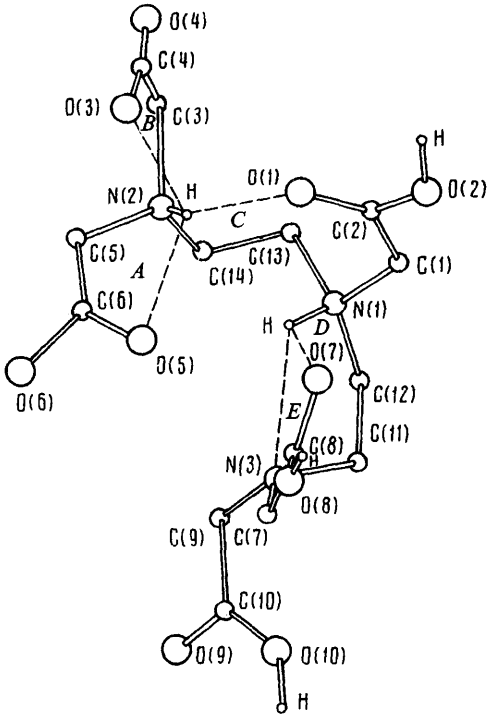


Figure 7. Structure of the diethylenetriamine-*N*,*N*,*N'*,*N''*,*N''*-pentaacetic acid (H_5dtpa) molecule.

Comparison of the H...O distances and angles at the H atoms in diamino complexes is perhaps not so indicative as in monoamino complexones, mainly because of the intervention of intermolecular O...H...O bonds that increase the lability of the hydrogen atoms. If the clear examples of this type of interference are set aside (indicated by additional symbols in brackets in the labelling of the H-rings in Table 4), all of the H...O distances in rings of the type $1\bar{c}$ or $2\bar{c}$ fall within the region of 2.00–2.38 Å and the angles at the H atom are 101–132° while in rings of the type 1*c'* the distances are in the range 2.17–2.52 Å and the angles are 94–124°. In the only "pure" 1*c''* ring the O...H distance and N–H...O angle are equal to 2.42 Å and 95° respectively, while in the only 1*h* ring these values are 2.41 Å and 106°. At any rate these results are not at variance with the series of H-acceptor activity which was put forward on the basis of the structures of monoamino complexones.

Bonds of the type C–H...O (H...O equal to 2.27, 2.35 and 2.37 Å) which are found in the diamino complexone H_8edtph are somewhat shorter than the analogous bonds in monamino acids, while the angles at the H atom are greater than 140°.

V. Prototropic tautomerism in aminocarboxylic complexones

In the crystal structures of some of the mono- and diaminocarboxylic complexones discussed and also in the triamino complexone H_5dtpa short intramolecular hydrogen bonds of the type O...H...O occur (usually slightly asymmetric) with an O...O distance in the range 2.43–2.49 Å and an angle at the H atom in the range 160–180°. In certain cases studies have revealed two possible positions of the hydrogen atom between the oxygens. Short H-bonds can combine acidic groups of neighbouring molecules into dimer pairs or chains.

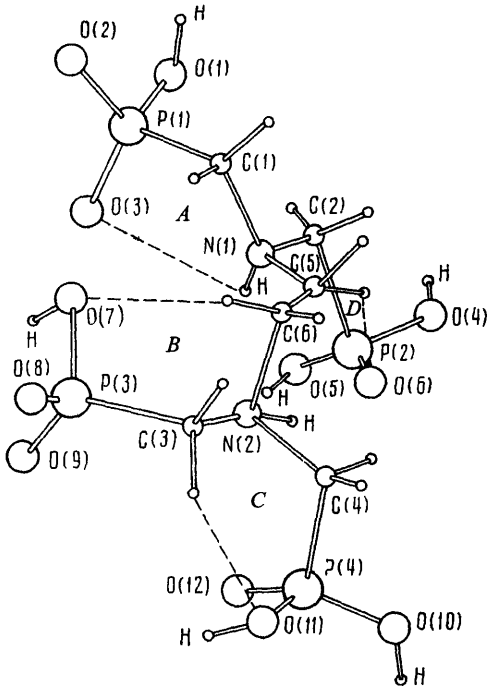
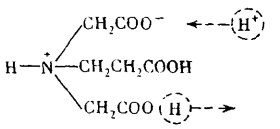


Figure 8. Structure of the ethylenediamine-*N*,*N*,*N'*,*N'*-tetramethylphosphonic acid (H_8edtph) molecule.

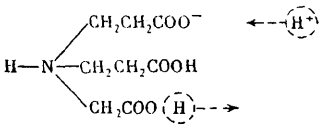
This fact suggests the possibility of tautomeric rearrangement in solution by migration of a proton or, at least, the possibility of two tautomeric forms existing in a given proportion. This suggestion is based on the somewhat unusual distribution of hydrogen atoms amongst the acid groups and on the unexpected asymmetry of some complexones.

In crystals of nitrilopropionic diacetic acid (H_3npda) one of the acetate groups is deprotonated. At the same time there is a "short" O–H...O bond of length 2.460(4) Å between the CH_2COOH groups of one molecule and CH_2COO^- groups of another [see scheme (IX) and Fig. 2*c*]. The tautomeric rearrangement on migration of a proton does not give rise to any fundamental change in the chemical structure of the molecule—deprotonated and protonated acetate groups are preserved. It is different with the

structure of nitrilodipropionic acetic acid (H_3ndpa) [see scheme (X) and Fig. 2*b*]:

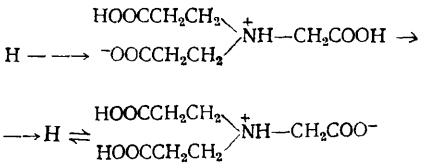


(IX)



(X)

It is somewhat surprising that in the presence of the more acidic acetate group it is one of the propionate groups that is actually deprotonated. However, the short hydrogen bond of length 2.467(8) Å between the hydrogen atom of a CH_2COOH group and the oxygen atom of a $CH_2CH_2COO^-$ group suggests the possibility of a tautomeric rearrangement occurring when the molecule passes into solution to form a more stable zwitterion form:



In the structure of the semi-open diamino complex H_4dhobta (see Fig. 4*c*) the asymmetry in the arrangement of CH_2COO^- and CH_2COOH groups (two CH_2COO^- groups are situated on the N atom and two CH_2COOH groups are on the N* atom) is unexpected. However, there is a short intermolecular hydrogen bond O(4)*—H(O4)*...O(2) between the O(4)* and O(2) atoms of neighbouring molecules. The O(4)*...O(2) distance is equal to

Table 4. Geometric properties of N—H...O and N—H...N hydrogen bonds in the structures of diaminocarboxylic, triaminocarboxylic, and diaminophosphonic complexones, anions, and cations.

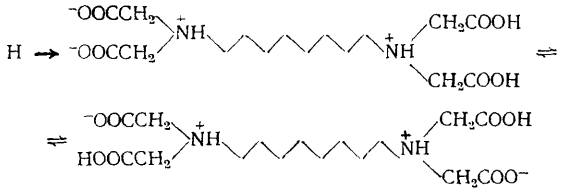
Complexone, anion or cation	Labelling of H-ring or IEHB	Geometry of N—H...O(N) bond				Sets of H-bonds
		Distance, Å			N—H...O (N—H...N) angle, deg	
		N—H	H...O (H...N)	N...O (N...N)		
H_2eddp·$2H_2O$	$1\bar{c}_2$	0.95(3)	2.56(4)	3.119(5)	118(2)	$1\bar{c}_2$-IEHB
	IEHB	0.95(3)	1.87(4)	2.774(5)	157(2)	
	IEHB	1.07(3)	1.61(4)	2.662(5)	165(2)	IEHB
H_2oadp	1*c*′	0.85(4)	2.30(4)	2.711(4)	110(3)	1*c*′-IEHB
	IEHB	0.85(4)	2.21(4)	3.010(4)	156(3)	
oadp^{2-} in [Cu(oadp)(bipy)$(H_2O)_2$]H_2O (Ref.19)	1*c*′	0.86(3)	2.30(3)	2.683(3)	107(4)	1*c*′-IEHB
	IEHB	0.86(3)	2.19(3)	2.918(3)	143(4)	
	1*c*′	0.76(3)	2.50(3)	2.781(3)	104(3)	1*c*′-IEHB
	IEHB	0.76(3)	2.15(3)	2.861(3)	157(3)	
H_4dbata·$2H_2O$	$1\bar{c}$(1*c*″)	0.90(2)	2.46(3)	2.687(3)	95(2)	$1\bar{c}$-1*c*′-IEHB (1*c*″-1*c*-IEHB)
	1*c*′($1\bar{c}$)	0.90(2)	2.24(3)	2.714(3)	113(2)	
	IEHB	0.90(2)	2.18(2)	2.877(3)	134(2)	
H_4dbeta·$2H_2O$	$1\bar{c}$(1*c*″)	0.87(3)	2.53(3)	2.707(3)	92(2)	$1\bar{c}$-1*c*′-IEHB (1*c*″$1\bar{c}$-IEHB)
	1*c*′($1\bar{c}$)	0.87(3)	2.22(3)	2.703(2)	115(2)	
	IEHB	0.87(3)	2.14(3)	2.838(2)	137(3)	
H_4dhobta·$2H_2O$	$1\bar{c}$	0.91(3)	2.23(2)	2.672(3)	106(2)	$1\bar{c}$-$1\bar{c}$-1*h* ($1\bar{c}$-1*c*′-1*h*)
	$1\bar{c}$(1*c*′)	0.91(3)	2.03(2)	2.628(3)	122(2)	
	1*h*	0.91(3)	2.41(2)	2.804(3)	106(2)	
	1*c*′	0.98(3)	2.33(3)	2.723(3)	103(2)	1*c*′-1*c*′-IEHB ($1\bar{c}$-1*c*′-IEHB)
	1*c*′($1\bar{c}$)	0.98(3)	2.11(3)	2.652(3)	113(2)	
	IEHB	0.98(3)	2.24(3)	3.011(3)	135(2)	
H_4egta	1*c*′	0.89(3)	2.27(2)	2.217(3)	111(2)	1*c*′-1*c*′-IEHB
	1*c*′	0.89(3)	2.45(2)	2.746(2)	100(1)	
	IEHB	0.89(3)	2.11(2)	2.862(2)	142(2)	
H_4edta	$1\bar{c}$(1*c*′)		2.33(3)	2.748(2)	108	$1\bar{c}$-1*c*′-$2\bar{c}$ ($1\bar{c}$-1*c*′-2*c*′)
	2*c*(2*c*′)		1.95(3)	2.787(2)	152	
	1*c*′($1\bar{c}$)		2.39(3)	2.682(2)	99	

Table 4 (cont'd).

Complexone, anion or cation	Labelling of H-ring or IEHB	Geometry of N–H...O(N) bond				Sets of H-bonds
		Distance, Å			N–H...O (N–H...N) angle, deg	
		N–H	H...O (H...N)	N...O (N...N)		
H_2edta^{2-} in $[K_2H_2edta)].2H_2O$ (Ref.41)	$1\bar{c}$			2.610		$1\bar{c}$-$1\bar{c}$-$2\bar{c}$
	$1\bar{c}$			2.512		
	$2\bar{c}$			2.928		
	$1\bar{c}$			2.736		$1\bar{c}$-$1\bar{c}$-$2\bar{c}$
	$1\bar{c}$			2.809		
	$2\bar{c}$			2.714		
H_2edta^{2-} in $[Mg(H_2O)_6](H_2edta)$ (Ref.42)	$1\bar{c}$	0.89	2.38(2)	2.708(2)	102	$1\bar{c}$-$1\bar{c}$-IEHB
	$1\bar{c}$	0.89	2.18(2)	2.660(2)	113	
	IEHB	0.89	2.22(2)	2.899(2)	132	
H_2edta^{2-} in $Rb_2(H_2edta).2H_2O$ (Ref.43)	$1\bar{c}$			2.61		$1\bar{c}$-$1\bar{c}$-IEHB
	$1\bar{c}$			2.63		
	IEHB			2.63		
	$1\bar{c}$			2.60		$1\bar{c}$-$1\bar{c}$-IEHB
	$1\bar{c}$			2.74		
	IEHB			2.96		
H_5edta in $[H_5edta]Br.H_2O$ (Ref.39)	$1\bar{c}(1c'')$	0.90(7)	2.40(6)	2.646(5)	96(5)	$1\bar{c}(1c')$-$1c'$-IEHB
	$1c'$	0.90(7)	2.18(6)	2.718(5)	118(6)	
	IEHB(Br)	0.90(7)	2.61(7)	3.282(6)	132(6)	
	$1c''(1\bar{c})$	0.85(7)	2.42(6)	2.651(5)	95(5)	$1c''(1\bar{c})$-$1c'$-IEHB
	$1c'$	0.85(7)	2.17(6)	2.700(6)	120(6)	
	IEHB	0.85(7)	2.18(7)	2.847(7)	134(6)	
H_6edta^{2+} in $[H_6edta]Cl.3H_2O$ (Ref.44)	$1c'$	1.06	2.20	2.69(2)	106(8)	$1c'$-$1c'$-IEHB
	$1c'$	1.06	2.41	2.67(2)	104(8)	
	IEHB(Cl)	1.06	2.35	3.17(1)	133(7)	
	$1c'$	1.10	2.07	2.70(2)	114(8)	$1c'$-$1c'$-IEHB
	$1c'$	1.10	2.48	2.71(2)	90(8)	
	IEHB(Cl)	1.10	2.34	3.15(1)	129(7)	
$H_4edds \cdot 5H_2O$	$1\bar{c}$		2.20	2.668	107	$1\bar{c}$-$1c_2'$-$2\bar{c}$
	$2\bar{c}$, $1c_2$		2.20	2.784, 2.952	132	
$H_4cdta \cdot H_2O$	$1c$	0.99(4)	2.27(4)	2.652(4)	101(2)	$1\bar{c}$-$1c'$-$2e$
	$1c'$	0.99(4)	2.52(4)	2.771(4)	94(2)	
	$2e$	0.99(4)	2.25(4)	2.825(3)	116(3)	
H_6cdta^{2+} in $[H_6cdta][PdCl_4].5H_2O$ (Ref.45)	$1c'$			2.718		$1c'$-$1c'$-$2c'$
	$1c'$			2.662		
	$2c'$			2.858		
	$1c'$			2.723		
	$1c'$			2.693		$1c'$-$1c'$-$2c'$
	$2c'$			2.894		
H_5dtpa	$2e$	0.95(4)	2.23(4)	2.830(3)	120(3)	$2ec'$
	$1c'$	0.95(4)	2.34(4)	2.975(3)	124(3)	
	$1\bar{c}$	0.91(4)	2.21(4)	2.673(3)	111(3)	$1\bar{c}$-$1c'$-$2\bar{c}$ ($1\bar{c}$-$1c$-$2c'$)
	$2\bar{c}(2c')$	0.91(4)	2.24(4)	2.991(4)	140(3)	
	$1c'(1\bar{c})$	0.91(4)	2.46(4)	2.696(3)	95(3)	
$H_4eddph \cdot 2H_2O$	$1\overline{ph}''$	0.83(6)	2.68(5)	2.885(4)	96(5)	$1\overline{ph}''$-IEHB
	IEHB	0.83(6)	1.97(6)	2.733(5)	154(5)	
	IEHB	0.87(5)	1.86(5)	2.693(5)	162(5)	IEHB
$H_4eddiph \cdot 2H_2O$*	$1\overline{ph}'$	1.06(10)	2.27(10)	2.812(17)	110(7)	$1\overline{ph}'$-IEHB
	IEHB	1.06(10)	1.99(11)	2.944(19)	148(8)	
	IEHB	1.27(16)	1.38(16)	2.618(20)	162(9)	IEHB
$H_6eddiph^{2+}$ in $[H_6eddiph]Cl_2.2H_2O$ (Ref.29)	$1\overline{ph}'$	0.97(4)	2.51(4)	2.882(3)	103(2)	$1\overline{ph}'$-IEHB
	IEHB	0.97(4)	1.86(4)	2.801(3)	163(3)	
	IEHB(Cl)	0.87(4)	2.28(4)	3.126(3)	168(3)	IEHB
$H_8edtph \cdot H_2O$	$1\overline{ph}'$	0.79(4)	2.61(4)	2.970(4)	110(3)	$1\overline{ph}'$-IEHB
	IEHB	0.79(4)	1.98(4)	2.733(4)	160(4)	
	IEHB	0.81(3)	1.90(3)	2.689(4)	163(3)	IEHB

*Random distribution of O atoms of phosphonic groups.

2.470(2) Å, the H-bond is almost symmetrical, and the C–O bonds in the groups that are linked are evidently capable of undergoing tautomeric rearrangement by delocalisation of π-interaction. In the O(1)–C(2)–O(2) group they are equal to 1.228(4) and 1.266(3) Å respectively while in the O(3)*–C(4)*–O(4)* group they are 1.217(3) and 1.293(3) Å in length. Under these conditions it is natural to expect a tautomeric change to a symmetrical form on solution:



Short O–H...O IEHB also occur in a number of closed diamino complexones, and primarily in H_4edta itself (Fig. 5*b*). The O(4)...O(2) distance in short IEHB is equal to 2.460(2) Å, and the O(4)–H and O(2)...H distances are 1.20(3) and 1.28(3) Å. It is the acetate groups that are able to undergo rearrangement (see Fig. 5*b*). In the COOH group the π-electrons are not completely localised and in the COO^- group they are delocalised. When tautomeric rearrangement occurs in both halves of the molecule the $1\bar{c}-1c'-2\bar{c}$ sets of H-rings are changed to $1c'-1\bar{c}-2c'$. The molecular symmetry as a whole is not disturbed.

The asymmetric structures of the diamino H_4cdta and triamino H_5dtpa complexones are the most interesting in relation to the present topic. It is not difficult to see (see Fig. 6*a*) that the position of one of the carboxyl groups bonded to the non-protonated N(2) atom [the group containing the O(8) and H(O8) atoms] is such that the molecule as a whole is capable of forming an O(8)...H(N1)–N(1) bond. Although the O(8)–H(N1) distance is quite long (2.62 Å), a small change in the conformation of the central section could lead to cleavage of the N(1)–H(N1)...N(2) bond and formation of an N(1)–H(N1)...O(8) bond with replacement of the $1\bar{c}-1c'-2e$ set by a $1\bar{c}-1c'-2c''$ set. If a subsequent tautomeric transfer of the H(O8) proton from the O(8) atom to N(2) is assumed, the complex would acquire a symmetrical structure similar to that of H_4edta, with $1\bar{c}-1c'-2\bar{c}$ sets (see Fig. 6*b*).

Such a possibility is supported by the completely symmetrical closed structure of the H_6cdta^{2+} cation, in which both nitrogen atoms are quaternised. Since the synthesis of $[H_6cdta]^{2+}[MCl_4]^{2-}$ complexes, where M = Pd and Pt, occurs in hydrochloric acid solutions, we can suggest the nature of the changes in the structure of H_4cdta on going from a less acidic medium to a more acidic one.

The N...N distances in H_4edta, H_6cdta^{2+}, and H_4cdta are equal to 3.195, 3.102, and 2.825 Å respectively. It may be assumed from the similarity in the general conformation of these three molecules that under certain conditions H_4edta may undergo a reverse tautomeric rearrangement, i.e., acquire the asymmetric structure characteristic of H_4cdta.

In the triamino complexone H_5dtpa both the tautomeric rearrangement characteristic of H_4edta and a rearrangement similar to that described above for H_4cdta are possible.

In fact, H_5dtpa molecules are combined in the crystalline state through the formation of IEHB similar to that found in H_4edta crystals. The O(2)...O(4) distance (between the carboxyl and carboxylate groups of neighbouring molecules) is equal to 2.455(3) Å with O...H* distances (1.24–1.25 Å) that are the same within the limits of experimental error. It is the acetate groups which are capable of undergoing rearrangement. Transfer of a proton from O(2) to O(4) does not, of course, disturb the trifurcate IAHB involving the ammonium H(N2) atom, but it changes the $1\bar{c}-1\bar{c}-2c'$ set of H-rings to $1\bar{c}-1c'-2\bar{c}$, which is exactly the same as the set in H_4edta.

The position of one of the carboxyl groups on the non-quaternised N(3) atom in H_5dtpa (it is determined from the values of the dihedral angles) is very similar to the position of the analogous group in H_4cdta, but while in H_4cdta the O(8) atom is merely capable of forming an O(8)...H(N1)–N(1) bond, in H_5dtpa the analogous O(7) atom forms such a bond and completes an eight-membered ring (in this case an H-ring of the type $2ec'$). It is also possible to admit the transfer of the H(O8) proton in the H_5dtpa molecule on to the N(3) atom with replacement of the bifurcated $2ec'$ system (containing a $2c'$ ring as a component) by a $2c'$ with an N(1)–H(N1)...O(7) bond and a $1c'$ ring with an N(3)–H(N3)...O(7) bond and with a suitable rotation of the carboxyl group containing the O(9) and O(10) atoms leading to the formation of a second ring of the type $1c'$ with an N(3)–H(N3)...O(9) bond (compare ring *D* in Fig. 6*b*).

Of course, these rearrangements can only be regarded as conjectural, but on the whole the possibility of the occurrence in complexones of tautomeric rearrangements relating to the position of "active" H atoms between different acidic groups of neighbouring molecules or to incomplete quaternisation of N atoms clearly exists.[4]

Table 5. List of monoamino and diamino complexone hydrohalides.

Name	Standard notation	Refs.
Iminodiacetic acid monohydrofluoride monohydrate	$[H_3ida]F\cdot H_2O$	[49]
Iminodiacetic acid monohydrochloride	$[H_3ida]Cl$	[50]
Iminodiacetic acid monohydrobromide	$[H_3ida]Br$	[50]
Iminodiacetic acid monohydroiodide	$[H_3ida]I$	[51]
Ethylenediamine-*N,N'*-dipropionic acid dihydrochloride	$[H_4eddp]Cl_2$	[39]
Ethylenediamine-*N,N,N',N'*-tetrapropionic acid dihydrochloride	$[H_6edtp]Cl_2$	[39]
Ethylenediamine-*N,N,N',N'*-tetraacetic acid dihydrochloride trihydrate	$[H_6edta]Cl_2\cdot 3H_2O$	[44]
Ethylenediamine-*N,N,N',N'*-tetraacetic acid monohydrobromide monohydrate	$[H_5edta]Br\cdot H_2O$	[39]
Phosphonomethylglycine semihydrochloride	$H_3phmg\cdot {}^1/_2HCl$	[15]
Ethylenediamine-*N,N'*-diisopropylphosphonic acid dihydrochloride dihydrate	$[H_6eddiph]Cl_2\cdot 2H_2O$	[29]

VI. Structural features of hydrohalides of complexones

The structures of hydrohalides of complexones can be used to simulate the behaviour of the corresponding complexones in strongly acidic media.[4] At the present time structural data on eight hydrohalides of aminocarboxylic complexones and two hydrohalides of aminophosphonic complexones are available (Table 5). These data relate to four hydrohalides of H_2ida (including its

hydrofluoride), dihydrochlorides of two acids containing propionate groups (H_2eddp·2HCl and H_4edtp·2HCl), and two hydrohalides of H_4edta (H_4edta·HBr·H_2O and H_4edta·2HCl·$3H_2O$), as well as phosphonomethylglycine semihydrochloride H_3phmg·½HCl and the dihydrochloride of ethylenediamine-*N*,*N*′-di(isopropylphosphonic) acid H_4eddiph·2HCl·$2H_2O$. The position of the dissociated protons of hydrohalic acids is a key feature in a discussion of the structure of compounds of this class.[4] In this case it is logical to start with the concept of a zwitterion structure of complexones in both the crystalline state and solution.

It was possible to use the structural data to establish a dependence of the crystalline structure of hydrohalides of complexones on the acidic properties of the functional groups. In cations based on weak acids the dissociated protons of the hydrohalides are clearly located on the deprotonated acid groups of the complexones, converting the molecules of the latter into cations. Strong (according to the classification of Megaw)[46] IAHB does not occur in such crystals. As an example let us examine the structure of the propionates H_2eddp·2HCl and H_4edtp·2HCl, for which precisely this type of cation-anion structure—$(H_4eddp^{2+})(Cl^-)_2$ and $(H_6edtp^{2+})(Cl^-)_2$—has been found. The cations have an open structure with the protons (from HCl) quite clearly located on the propionate groups. Although the latter could potentially participate in IAHB to form $1c'_2$ or $1c''_2$ H-rings, such rings do not occur. Even though the cations have an open structure they cannot form IEHB either between themselves or with anions.

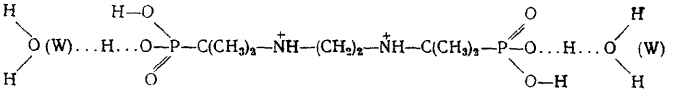
A similar cation-anion structure also occurs for hydrohalides of H_2ida, although the acetate groups have a higher acidity than propionate groups. The absence of acceptors that are suitable for forming strong IEHB, which is supported by the completely different structure of H_2ida hydrofluoride (see below), may in this case account for the low strength of IEHB.

In cations based on fairly strong acids, the dissociated protons of the hydrohalides, on the other hand, participate in the formation of strong IEHB of the type O—H...O or O—H...X, with H-rings based on IAHB being retained, although it is true that they are sometimes in combinations that are different from those in the initial complexones. Different situations can occur depending on the nature of the acid group.

Thus in H_2ida hydrofluoride quite strong IEHB of the type O—H...F has been detected between the O atom of the carboxyl group and an F^- ion [O...F distance is 2.502(2) Å], which can be attributed to the closeness of their electronegativity values (and also the van der Waals radii), i.e., to satisfy the conditions that are necessary for the formation of strong bonds.[47] A similar pattern, namely, conversion of the complexone to a cationic form with the formation of more or less strong IEHB of the type O—H...O [length 2.51(2) Å], also occurs in the case of the above-mentioned H_4edta·2HCl·$3H_2O$, the actual formula of which is $(H_6edta^{2+})(Cl^-)_2 \cdot 3H_2O$ (1:2 composition). Protonation of all of the acid groups in the complexone eliminates its zwitterion character.

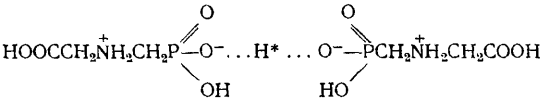
The formation of a cationic form in the hydrobromide H_4edta·HBr·H_2O (1:1 composition) occurs in a different manner. Conversion of the H_4edta molecule into an H_5edta cation does not destroy the zwitterion character of the molecule, but with this type of protonation its structure changes markedly, as has already been mentioned. The crossed eight-membered H-rings are ruptured and the central section acquires a transoid structure. At the same time the proton from dissociated HBr is not attached to any single CH_2COO^- group but is located between "semi-protonated" acetate groups of neighbouring complexones, forming strong IEHB of the type O(1)...H*...O(1)* (Fig. 5*a*) of length 2.455(5) Å with a random arrangement of two positions that are separated from each other by 0.66 Å. The resulting infinite associate that is based on this type of IEHB may be regarded as both a chain of H_5edta^{2+} cations and an alternating sequence of neutral H_4edta molecules and H_6edta^{2+} cations. It is also worth drawing attention to the fact that synthesis of this compound was carried out using excess HBr; hence the composition of the product depends on the nature of the halogen (compare with H_4edta hydrochloride).

A similar situation occurs in the structure of H_4eddiph·2HCl·$2H_2O$, where the protons from HCl are randomly distributed between monoprotonated phosphonate groups and water molecules through a strong IEHB of length 2.423(4) Å.



In this case such a structure also proves possible for a composition of 1:2 because of the increased acidity of the phosphonic group compared to the carboxyl; the pK_1 values of H_2ida and H_4idph acids are 2.54 and < 1 respectively.[48] Attachment of the proton to one of the O atoms participating in the formation of IEHB can indicate two structural variants in this case: combinations of zwitterion H_4eddiph molecules and H_3O^+ and Cl^- ions or combinations of H_6eddiph^{2+} cations, water molecules, and Cl^- anions. As in the case of H_4eddiph·$2H_2O$, the complexone in H_4eddiph·2HCl·$2H_2O$ retains a semi-open structure.

In the structure of the hydrochloride H_3phmg·½HCl, the proton that has dissociated from HCl unites two H_3phmg molecules into a dimeric associate



with a strong symmetrical IEHB O...H*...O of length 2.454(3) Å. The structure in this case is quite unambiguous; the H* protons are situated at the centres of inversion and the Cl^- anions are on double axes of symmetry. In the H_3phmg hydrochloride molecule a $1c'$ H-ring is retained and the $1\overline{ph}'$ H-ring present in the structure of H_3phmg itself has opened.

The small amount of data on the crystalline structures of hydrohalides reported in this section shows that both their composition and structure are determined primarily by the nature (acidic properties) of the functional groups of the complexone and to a considerable extent by the nature of the halogen.

VII. Conclusion

The role of crystal chemical data in the resolution of problems in basic chemistry has increased very greatly during the last ten years. Structural analysis has been introduced into the very fabric of chemical research as one of its most indispensable and important components. The significance of this component is especially great for those areas of chemistry which deal with structural units—molecules, oligomers, or polymers—consisting of residues that can undergo various ways of combining with each other.

On the preceding pages only one aspect of the structural chemistry of complexones was examined—the structure of the

molecules themselves. Questions relating to the packing of the molecules in crystals, the geometric ratios with the outer-sphere ions and solvate (hydrate) molecules have been referred to only occasionally by the present authors, in mentioning only those cases of interest for their unusual nature or of importance for an understanding of possible rearrangements on going from the crystalline state to solution.

There is no doubt that there are many different aspects of the structure of such complex compounds as polyaminopolycarboxylic acids that have not been touched upon in this review. But in any case there seems to be no doubt that even incomplete structural data on complexones are not solely of independent interest. To an even greater degree they are important as a structural basis for the interpretation of their spectroscopic parameters and for developing the most effective and adequate theoretical ideas about the relationship between structural and spectroscopic properties, for a comparison of the structure of complexones and metal complexonates in crystals and in solution under different conditions (depending on the concentration and acidity), and in the end they are important for a better understanding of reaction pathways and for directed synthesis of complexonates in solving specific practical problems. The present authors, however, have quite deliberately limited the scope of this study to purely structural material, in realising that all of these problems require further varied and thorough physicochemical studies and that to supply the overall results in this area is premature for the time being.

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Spiropyrans: structural features and photochemical properties

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ABSTRACT. The structure of photochromic systems based on different classes of spiropyrans, which are promising materials for the optical recording of information and control of luminous fluxes is examined. The structural factors which affect the photochemical activity of spiropyrans and the stability of the coloured forms derived from them have been established. It is shown that the photochemical properties of spiropyrans occurs to a considerable extent because even in the ground state the $C_{spiro}-O$ bond being cleaved on photoexcitation is weakened and elongated through specific $n-\sigma^*$ orbital interactions. The effect of the nature, electronic state, and relative orientation of the heteroatoms in the spiro centre on the efficiency of $n-\sigma^*$ interactions is analysed. The formation of different strong intermolecular associates and solvates has been found in the crystalline structure of the coloured forms of spiropyrans, which to a considerable degree determines the stabilisation of the complex resonance structure of these compounds.

The bibliography includes 92 references.

Contents

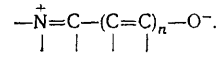
I. Introduction 663
II. Structure of indoline spiropyrans 664
III. Structure of open merocyanine forms of indoline spiropyrans 671
IV. Effect of the nature and relative orientation of the heteroatoms in the spiro centre on the structure and photochemical properties of spiropyrans 677
V. Structure, photo- and thermo-chromic properties of 2-oxaindan spiropyrans with polycondensed chromene residues 679
VI. Conclusion 683

I. Introduction

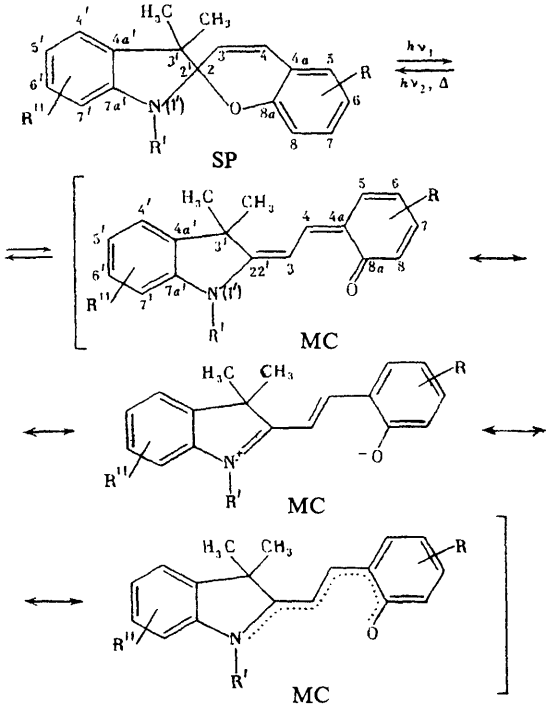
Photochromic materials based on different classes of spiropyrans (SPs) are widely used at the present time for the production of light filters that regulate luminous fluxes, photochromic organic media for recording and processing optical information, and in other areas of science and technology.[1] Among the different classes of photochromic materials, indoline spiropyrans are distinguished by their high sensitivity and resolving power, and they exhibit photochromic properties in solution, in polymer matrices, and even in the solid state, which is very convenient for their practical application.

Photolysis of virtually colourless spiropyrans leads to the formation of dyes, the electronic absorption spectra of which occur in the region of ~400 to 700 nm and have a complex pattern that depends on the structure of the SP, the nature and position of the substituents, the solvents, the temperature, and other factors. Many SPs also have thermochromic properties. Despite intensive research in this field, the mechanism of photochromic SP reactions and the relationship between their structure and photochemical properties are still not fully understood.

It was established[2,3] from spectroscopic and quantum-chemical data that photo- and thermal coloration of indoline SPs is due to a valence isomerisation related to cleavage of the $C_{spiro}-O$ bond and formation of a merocyanine type of coloured structure



The photochemical activity of an SP can depend to a considerable extent on the energy of the $C_{spiro}-O$ bond and its polarity,[4] the charge distribution on the atoms of the pyran ring,[5] and the degree of electronic interaction between the indoline and pyran sections of the molecule.[6–8] The stability of the resulting merocyanine (MC) and its spectroscopic properties are related to the degree of planarity of the chromophoric chain,[9] the presence of intramolecular H-bonds stabilising the structure,[10] and the degree of equivalence of the orders of π-bonds in the chromophore.[11] These factors, which affect the photochemical properties of SPs, primarily depend on the structure of the initial SPs and the resulting MC forms.



Therefore a systematic X-ray study of these compounds is important not only for an understanding of the structural mechanism of the photochromic reactions of SPs but also for establishing the relationship between their structure and photochemical properties.

At the present time the synthesis of SPs of practical importance is related to a varied structural modification of these systems which improves their performance characteristics, such as quantum yield of photolytic conversions, lifetime of the open form, and a high number of conversion cycles without substantial decomposition of the SP. Nevertheless, X-ray diffraction studies on SPs only started in the middle of the 1970's.[12,13]

II. Structure of indoline spiropyrans

1. Effect of structure on photochemical properties

An X-ray diffraction study of the initial 1',3',3'-trimethyl-6-nitro-8-bromospiro(indoline-2,2'-[2*H*-1]benzopyran) [SP(I)] (R' = CH_3, R^6 = NO_2, R^8 = Br) and its photochemical conversion product—MC(I)—was first successfully carried out in 1980.[14] Spiropyran SP(I) has thermochromic properties and at room temperature in solution is in equilibrium with its open form. Spiropyran (I) was obtained as yellow crystals by crystallisation from toluene on irradiation with light from an incandescent lamp. The photoproduct MC(I) was isolated from ethanol as dark red crystals. The general shape of the SP(I) molecule is shown in Fig. 1. The nonplanar indoline and benzopyran residues are situated approximately at right angles to each other in the molecule. The indoline residue has a dihedral angle of 27° along the line of N(1')...C(3'), and the benzopyran residue has a dihedral angle of 16.1° along the ling of O(1)...C(3) and 6.6° along the line of O(1)...C(4). The dihedral angle between the O(1)C(22')C(3) plane of the benzopyran ring and N(1')C(22')C(3') plane of the indoline ring at the C(22') spiroatom is 87.2°. The bond lengths and bond angles in the SP(I) molecule are similar to the corresponding values in spiropyrans SP(II) and SP(III) which were studied previously (II: R' = Ph, R^8 = NO_2;[12] III: R' = Ph, R^6 = Cl, R^8 = NO_2 [13]). In spiropyrans SP(I)–SP(III) the C_{spiro}–O bond [1.492(3)–1.496(4) Å] is considerably longer than normal C–O bonds in six-membered oxygen-containing heterocycles [1.41(1)–1.43(1) Å].[15–17]

The general shape of the MC(I) molecule is shown in Fig. 2. In crystals of MC(I) isolated from a solution of non-absolute alcohol, the MC(I) molecules are solvated with water molecules. The change

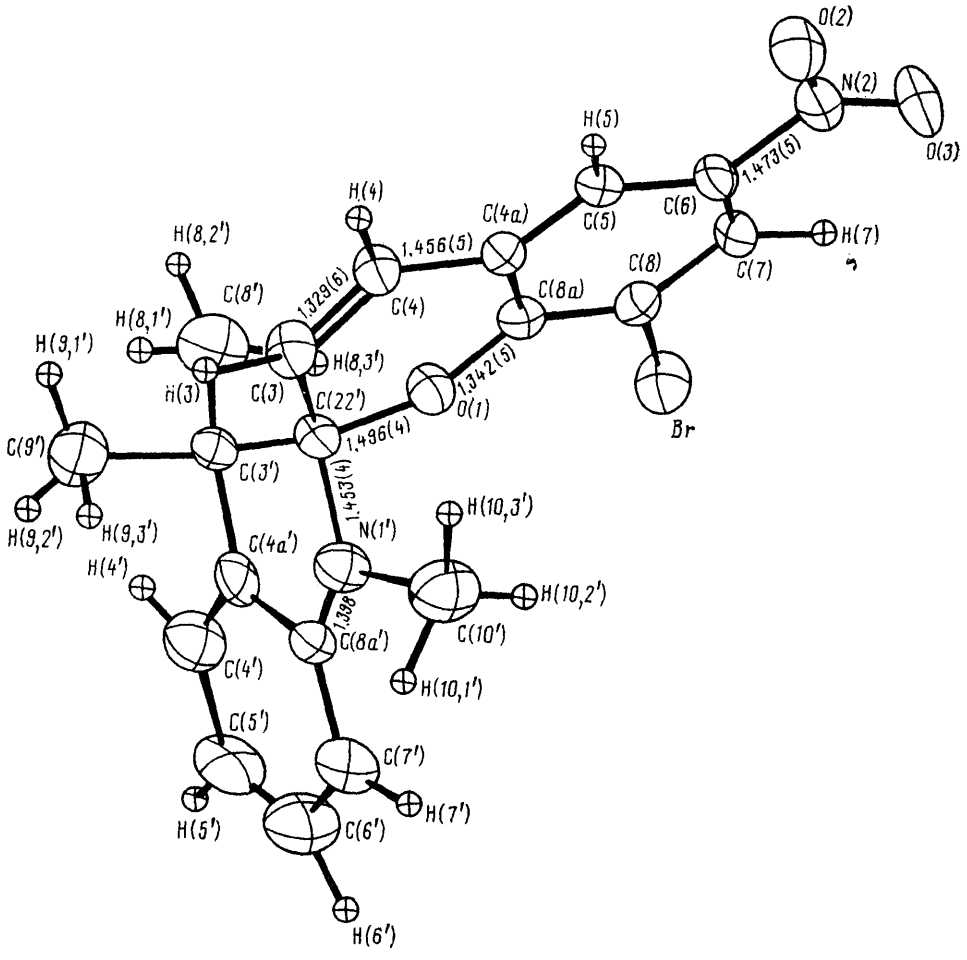


Figure 1. General shape of the SP(I) molecule.

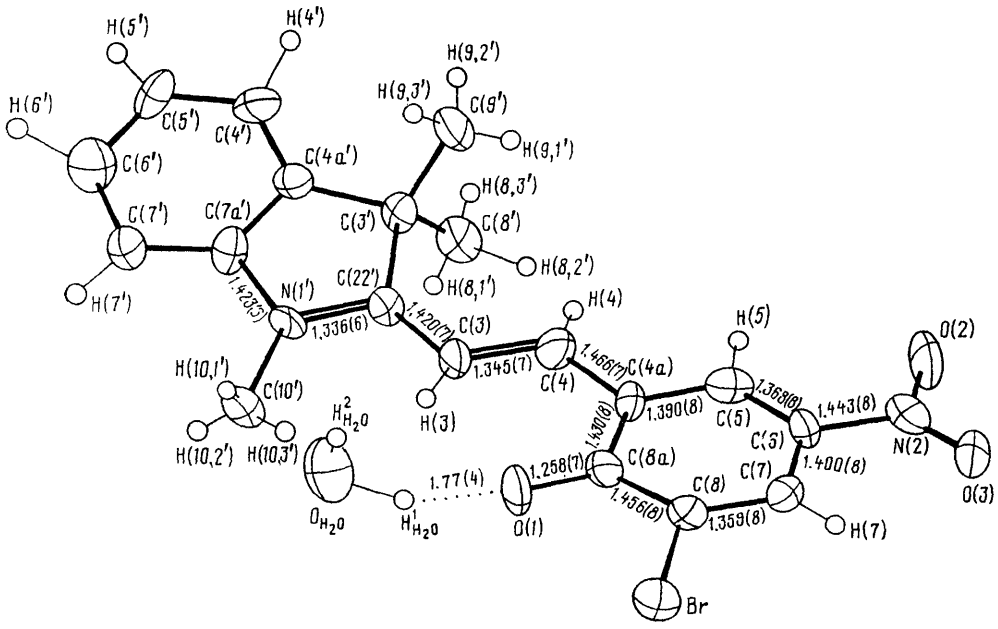


Figure 2. General shape of the MC(I) molecule.

to an open form is accompanied by a complete redistribution of bond lengths, typical for the merocyanine chromophore.[11] In this case the length of the single N(1')–C(22') bond, equal to 1.453 Å in SP(I), decreases to 1.336(6) Å in MC(I) and is of approximately the same magnitude as the length of a C=N double bond in five-membered heterocycles (1.29–1.33 Å).[15] The electrocyclic cleavage of the C_{spiro}–O(1) bond in SP(I) leads to a marked decrease in the length of the bond between the O(1) atom and the benzene ring in MC(I); the O(1)–C(8*a*) bond contracts to 1.258(7) Å. The length of this bond matches the length of the zwitterion bond in the *DL*-serine molecule, for example [1.26(1) Å].[15] The size of the C(4*a*)C(8*a*)C(8) bond angle in MC(I) [115.4(5)°] is considerably smaller than the usual value of 120°, which is an indication of the increase in σ-electron repulsion from the O(1) atom as a result of the localisation of a substantial negative charge on this atom. This type of distribution of bond lengths suggests that the MC(I) molecule has a bipolar structure [Fig. 3, form (A)]. On going from the closed form to the photoproduct the length of the C(6)–N(2) bond is reduced from 1.473(5) Å in SP(I) to 1.443(8) Å in MC(I) and at the same time the N(2)–O(2) and N(2)–O(3) bonds increase in length while the O(2)N(2)O(3) angle [122.3(6)°] decreases relative to the "equilibrium" value of 126.4° in aromatic nitro compounds[18] (see Figs. 1 and 2). This suggests that there is an increase in *s* character of the atomic orbitals of the N(2) atom participating in the formation of the C(6)–N(2) bond,[19] and is an indication of a strong resonance interaction between the NO_2 group and the benzene ring. The simultaneous elongation of the C(4*a*)–C(8*a*) and C(8*a*)–C(8) bonds and contraction of the C(7)–C(8) bond in the benzene ring (see Fig. 2) suggest that there is a significant contribution of the resonance quinoid form (B) to the structure of the *p*-nitrophenolate residue (Fig. 3).

It is also noticeable that the length of the C(5)–C(6) bond is reduced to 1.368(8) Å, which with the simultaneous contraction of the C(22')–C(3) bond [1.420(7) Å] compared to the length in SP(I) [1.483(5) Å] or even to the length of a single C_{sp^3}–C_{sp^3} bond (1.46 Å)[20] and some elongation of the C(3)–C(4) bond [1.345(7) Å] compared to the length of this bond in SP(I) [1.329(6) Å] indicate that there is an appreciable contribution of the resonance quinoid form (C) to the structure of MC(I) (Fig. 3). The mixing of structures (B) and (C) leads to delocalisation of electron density between the C(4a)–C(5) and C(5)–C(6) bonds and they decrease in length at the same time, consequently these bonds are shortened to a lesser degree than the C(7)–C(8) bond.

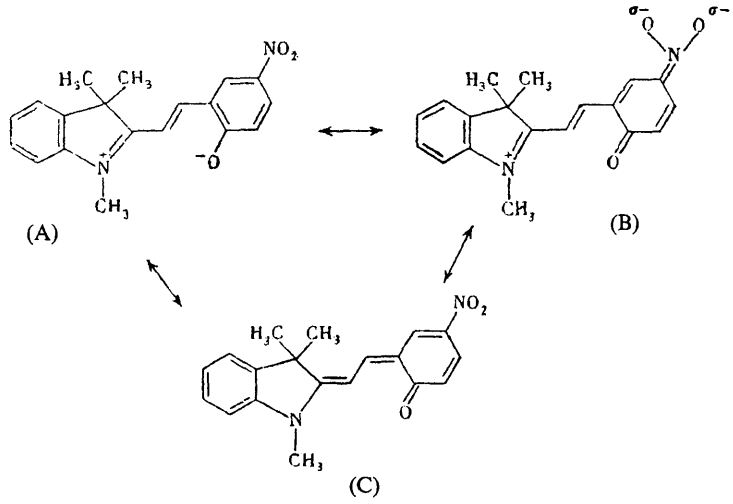


Figure 3. Resonance forms that mainly contribute to the structure of MC molecules.

Table 1. Main structural parameters of indoline spiropyrans SP(I)–SP(XI).

Spiropyran	Substituents			Bond lengths*1, Å				Angles, deg					Projection of the N(1′) atom from the plane of C(22′)–C(7a′)–C(R′)	Refs.
	R′	R″	R	C(22′)–O	C(22′)–N(1′)	O–C(8a)	N(1′)–C(7a′)	α	β*2	γ*2	τ	Δ		
(I)	CH_3	—	6-NO_2, 8-Br	1.496	1.453	1.342	1.398	27.0	16.1	6.6	169.5	160.2	0.26	[14]
(II)	C_6H_5	—	8-NO_2	1.492	1.432	1.356	1.413	30.7	−11.7	−3.3	169.6	126.4	0.13	[12]
(III)	C_6H_5	—	6-Cl, 8-NO_2	1.497	1.445	1.356	1.393	28.7	−17.1	−10.2	171.2	116.8	0.21	[13]
(IVa)*3	CH_3	—	6-NO_2	1.485	1.451	1.359	1.407	25.2	3.8	0	166.1	141.7	0.27	[23]
(IVb)*3	CH_3	—	6-NO_2	1.487	1.437	1.354	1.407	23.8	−15.5	−5.3	164.6	123.1	0.24	
(V)	CH_3	5′-NO_2	—	1.452	1.453	1.361	1.380	27.2	1.4	1.9	168.8	145.2	0.26	[24]
(VI)	CH_3	—	7-OCH_3	1.471	1.442	1.370	1.394	33.2	−14.6	−4.1	174.2	125.4	0.28	[29]
(VII)	C_6H_5	—	5,6-$C_6H_3NO_2$	1.460	1.450	1.372	1.416	28.5	−14.1	−0.8	168.2	129.7	0.12	
(VIII)	$CH_2C_6H_5$	—	6-NO_2	1.478	1.445	1.351	1.412						0.34	[25]
(IX)*3	CH_3	—	6-NO_2, 8-Br	1.486	1.434	1.333	1.386	29.9	−3.1	−1.6	169.5	139.6	0.29	[27]
(X)	CH_3	4′,5′-C_6H_4	6-NO_2	1.478	1.438	1.336	1.383	33.1	−3.2	0	171.5	141.8	0.30	[26]
(XI)	CH_3	—	4-Cl, 6-NO_2	1.479	1.438	1.343	1.402	29.7	0	1.5	170.0	141.3	0.30	[30]

Note. For numbering of the atoms, see Fig. 4, for angle notation, see text.

*1 Errors in determining the bond lengths constitute 0.003–0.006 Å.
*2 The positive angles correspond to a deflection towards the R′ substituent on the N(1′) atom, negative angles correspond to a deflection towards the *gem*-methyl groups on the C(3′) atom.
*3 Two independent molecules in the cell with a different structure.

The question concerning the presence of hydrogen bonds between the O(1) and H(3) atoms remains problematic. Even though the distance of O(1)...H(3) [2.28(5) Å] is short and the H(3) hydrogen atom, as follows from quantum-chemical calculations of charges on MC(I) atoms, must be fairly acidic, the small twist about the C(4)–C(4*a*) bond and the increase of the C(3)C(4)C(4*a*) bond angle to 127.4(5)° and C(4*a*)C(8*a*)O(1) bond angle to 125.0(6)° may indicate repulsion between the O(1) and H(3) atoms. A similar repulsion evidently occurs between the H(4) and C(3′) atoms, leading to an increase in the C(3)C(22′)C(3′) bond angle to 129.5° and the C(22′)C(3)C(4) angle to 123.9(5)° and an 11.7° twist about the C(22′)–C(3) bond.

Thus, the open form MC(I) has the zwitterionic, sterically most favourable, *trans*-cisoid structure (A) with some contribution from the resonance forms (B) and (C) (Fig. 3).

The X-ray diffraction studies carried out confirmed that when an SP molecule absorbs a quantum of light the C_{spiro}–O bond is cleaved in the pyran section of the molecule. The resulting sterically most favourable *trans*-cisoid isomer of MC is further stabilised in the crystalline state through the formation of hydrogen bonds with a molecule of water of crystallisation. Solvation of the O(1) oxygen atom of the phenolate residue in solution evidently also plays a significant role, which is confirmed, for example, by the increase in proportion of the photoform on going to more polar solvents.[21] Therefore it may be assumed that in solution, as in the crystalline state, that the isomer with the structure of MC(I) is the most stable of the possible isomers. This is supported by a spectroscopic study,[22] in which it is concluded that the *trans*-cisoid form is the most stable in solution.

In the SP molecule the C_{spiro}–O bond is elongated and is evidently the weakest. Therefore cleavage of the C_{spiro}–O bond in the SP molecule may in many respects be determined by this structural factor. Particular attention will be given subsequently to the following questions: 1) the structural factors that cause the C_{spiro}–O bond to increase in length; 2) correlation between the length of this bond, its strength, and the photochemical activity of the SP; 3) a detailed study of the structural factors which stabilise the photolytic form.

2. Specific $n-\sigma^*$ orbital interactions in indoline spiropyran molecules

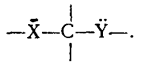
In this section the structural features of indoline SPs will be discussed in detail. The possible nature of the structural changes in the SP structure on photoexcitation and the effect of the structure on the quantum yield of photocoloration of these SPs are analysed, taking into account the orbital nature of the excited photochemically active states (PCAS).

a) Structural features of SP molecules in the ground electronic state

The main structural parameters of the SPs investigated are given in Table 1. In spiropyrans SP(I)–SP(IV)[12–14,23–30] the indoline and benzopyran residues of the molecules are approximately at right angles to each other but are not planar (Fig. 4). The indoline residue has the conformation of a flattened envelope with an inflection (dihedral angle α) along the line of N(1′)...C(3′) (dihedral angle α is in the range 23–30°, see Table 1). This type of structure for an indoline heterocycle is due to an essentially pyramidal

configuration of the N(1′) nitrogen atom, which reduces the conjugation between the unshared electron pair (UEP) of the N(1′) atom and the π-system of the benzene ring. In fact, the N(1′)–C(7*a*′) bond length in spiropyrans SP(I)–SP(XI), equal to 1.380(5)–1.416(5) Å, is greater than in corresponding systems with a planar trigonal structure of the N atom (1.36–1.37 Å), but matches the length of the N–Ph bond (1.39–1.42 Å) in molecules with a pyramidal structure of the N atom.[31–36] The projection of the N(1′) atom from a plane passing through the C(7*a*′) and C(22′) atoms and the carbon atom of the R′ substituent joined to the N(1′) atom is 0.12–0.34 Å. This is an indication of the substantial sp^3 character of the UEP of the N atom situated approximately perpendicular to the plane of these three atoms. The unshared electron pairs of the O atom are not equivalent;[37] they have a π- and σ-character and have different configurations. Thus, the UEP σ-electron density is situated in the plane of the C(22′)OC(8*a*) atoms while the UEP π-electron density occurs perpendicular to this plane. With such a structure of the SP the C_{spiro}–O bond of the pyran heterocycle occupies a *trans*-position relative to the UEP of the N(1′) atom and the C_{spiro}–N(1′) bond of the indoline heterocycle is *trans* relative to the π-UEP of the O atom. This type of structure can cause specific orbital interactions between the electronegative heteroatoms and the UEP of the N and O atoms bonded to a tetrahedral carbon atom (the anomeric effect).[38,39] This interaction may be described in terms of an n–σ* interaction between the UEP (n) of the heteroatom and the antibonding σ*-orbital of the adjacent polar bond located mainly on the positive carbon atom of the spiro centre[40] (Fig. 5). Since the electronegativity of the oxygen atom is greater than that of the nitrogen atom, and the UEP energy of the O atom is lower than the UEP energy of the N atom, the antibonding σ*-orbital of the C_{spiro}–O bond will be lower in energy than the antibonding orbital of the C_{spiro}–N(1′) bond, while the nonbonding orbital of the N(1′) atom will be higher in energy than the nonbonding orbital of the O atom. Consequently interactions between the n-electrons of the N(1′) atom and the σ*-orbital of the C_{spiro}–O bond are decisive in the spiro centre.[30]

Ideas about hyperconjugation have in recent years been widely used[41] to account for the structural consequences of the anomeric effect in different residues of the type



As a result of population of the antibonding orbital of the C_{spiro}–O bond, this type of interaction should lead to a strengthening of the C_{spiro}–N(1′) bond and a weakening of the C_{spiro}–O bond, which appears respectively as a contraction and elongation of these bonds. In fact, the C_{spiro}–N(1′) bond lengths in the SPs studied are in the range 1.432(4)–1.453(4) Å and prove to be considerably shorter than the normal lengths of C(sp^3)–N(sp^3) bonds (1.47–1.48 Å) in five-membered heterocycles,[15] while the C_{spiro}–O bond lengths are in the range 1.452(4)–1.497(5) Å and prove to be considerably longer than normal C–O bonds (1.41–1.43 Å)[15–17] in six-membered heterocycles.

The effectiveness of this hyperconjugation must depend to a considerable extent on the geometric configuration of the UEP of the N(1′) and O atoms and the C_{spiro}–O and C_{spiro}–N(1′) bonds on the one hand and the electronic state of the N and O atoms on the other hand. In all of the SPs studied the spiro centre has a sterically strained structure. Because of the rigidity of the tetrahedral structure of the spiro centre and the same conformation of the indoline ring, the C_{spiro}–O bond makes an angle (τ) of 165–171° with the UEP of the N(1′) atom (see Table 1).

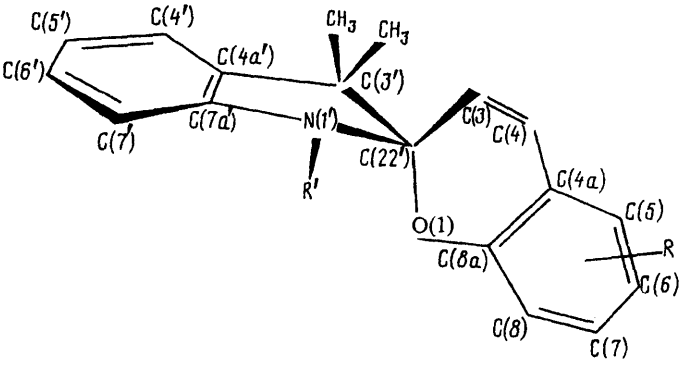


Figure 4. Schematic structure of SP molecules and the numbering of their atoms.

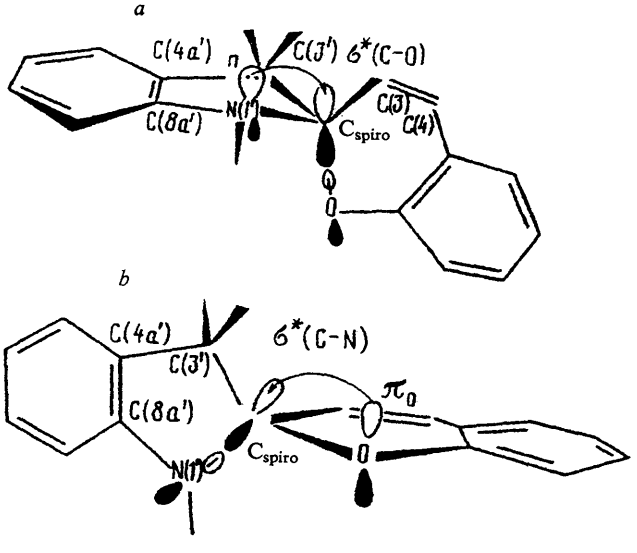


Figure 5. n[N(1)]–σ*(C_{spiro}–O) (*a*) and n(O)–σ*[C_{spiro}–N(1′)] (*b*) orbital interactions in SP molecules.

The conformation of the benzopyran residue is more flexible in these molecules. The pyran ring in an SP is nonplanar and is considerably folded along the line of O...C(3) (angle β) by 0–17° and less significantly along the line of O...C(4) (angle γ) by 0–10°. The conformation of the six-membered heterocycle in an SP is evidently determined by steric factors in the molecule and by packing effects of the molecules in the crystal rather than by the electronic effect of substituents. Confirmation of this is provided by the structure of SP(IV), in which in one of the independent molecules [SP(IV*a*)] the benzopyran ring is virtually planar while in the other [SP(IV*b*)] there are inflections with angles of 15.5° and 5.3°

respectively along the lines of O...C(3) and O...C(4). In spiropyrans SP(I), SP(IV*a*), and SP(V) the benzopyran residue is bent towards the R′ substituent while in spiropyrans SP(II), Sp(III), SP(IV*b*), SP(VI)–SP(X) it is bent towards the geminal methyl groups on the C(3′) atom.

The structural features described lead to a variable orientation of the π-electron density of the UEP of the O atom and the $C_{spiro}-N(1')$ bond (angle Δ, see Table 1). Thus in SP(II), SP(III), SP(IV*b*), SP(VI), and SP(VII) the angle between them is only 116–130°, in SP(IV*a*), SP(IX)–SP(XI) it is about 140°, and in SP(V) and SP(I) it is 145.2 and 160.2°. Thus, the $\pi(O)-\sigma^*[C_{spiro}-N(1')]$ interaction, which has an opposite effect to the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction, will strengthen with an increase in the angle Δ.

The electronic state of the N and O atoms depends on the nature and position of the substituents in the indoline and benzopyran residues. Introduction of an electron-acceptor (EA) molecule into the benzopyran residue at the *para*- and *ortho*-positions relative to the O atom should lead to an increase in conjugation of π-electron density of the UEP of the O atom with the benzene ring through further transfer of electron density from the O atom to the π-system of the phenyl group and the EA substituent. In fact, in spiropyrans SP(I) to SP(IV) and SP(VIII)–SP(XI) with EA substituents at these positions the O–C(Ph) bond lengths of 1.333(5)–1.357(5) Å and the C(Ph)–$N(NO_3)$ bond lengths of 1.459(5)–1.473(5) Å are shortened and similar to the lengths of the corresponding bonds in nitrophenols.[42,43] A decrease in electron density on the O atom causes a further polarisation of the $C_{spiro}-O$ bond, which leads to a decrease in energy of the σ*-orbital of the $C_{spiro}-O$ bond and its localisation on the C spiroatom to an even greater degree.[40] This helps to strengthen the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction and to further weaken and lengthen the $C_{spiro}-O$ bond compared to that in an unsubstituted SP, in which this bond must be stronger and shorter. Thus, as a result of specific orbital interactions in the photochromic indoline SPs, the $C_{spiro}-O$ bond, which is cleaved on photoexcitation, is the weakest and most elongated even in the ground state.

b) Nature of the structural changes in SP molecules during photoexcitation

The characteristics identified in the structure of SPs should have a substantial effect on the photochromic properties of these compounds. Since the photophysical and photochemical properties of organic molecules to a large extent depend on their structure in the excited state, we shall examine the nature of the structural changes in these molecules that take place on photoexcitation. The nature of such changes, in turn, depends on the type of electronic transition of the molecule in a photochemically active state (PCAS). The conversion of SP(I)–SP(IV) molecules to a PCAS on exposure to UV light with $\lambda > 300$ nm is caused by electronic transitions in the benzopyran part of the SP of the type $\pi l-\pi^*$ in molecules without EA substituents and of the type $\pi l-\pi^*\pi n^*$ in molecules with EA substituents in the benzopyran residue (see the review of Kholmanskii et al[44] and the references in it). It has been reliably established that these transitions constitute transitions with intramolecular charge transfer (ICT), mainly from the *l*-orbital of the oxygen atom and the π-orbital of the C(3)=C(4) bond to the phenyl group and the EA substitutent†.

† In this review[44] the π-orbital of the oxygen atom is identified as the *l*-orbital.

This ICT must lead to a decrease in electron density on the O(1) atom. Thus, for 2*H*-chromene it was found using the CNDO(S) method[45] that charge transfer from the O atom during the $S_0 \rightarrow S_3$ transition is 0.060 e. The decrease in charge on the O atom will be compensated by the σ-electrons of the $C_{spiro}-O$ bond, which should cause it to undergo further polarisation. As was shown above, this type of redistribution of electron density should lead to an increase in the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction in SP molecules and a further contraction of the $C_{spiro}-N(1')$ bond and weakening and elongation of the $C_{spiro}-O$ bond in the excited state. These conclusions are in agreement with the results of calculations using the MINDO-3 method on cleavage of the C–O bond of chromenes in an unexcited state.[46] It follows from the calculations that the length of the $C_{spiro}-O$ bond in the transition state, where cleavage of this bond occurs, is the same in all of the calculated molecules and constitutes ~1.95 Å. In the opinion of Simkin et al.,[46] the greatest proportion of the energy of activation for opening of the chromene rings is consumed on stretching the $C_{spiro}-O$ bond, the length of which at the initial stage of the reaction very accurately represents the reaction coordinate.

In spiropyran SP(V) the lowest electronically excited PCAS is the $^{1,3}(\pi l,\pi^*\pi n^*)$ state with ICT from the N(1′) atom to the phenyl residue and NO_2 group.[47] Therefore, the energy of the $n[N(1')-\sigma^*(C_{spiro}-O)$ interaction in the excited PCAS of SP(V) must be lower than in SP(IV), and the elongation of the $C_{spiro}-O$ bond in SP(V) is less than in SP(IV) (Table 1).

It has been shown[48] that a significant change in length of any bond in the excited state of the molecule assists the nonequilibrium transfer of electronic excitation energy of the molecule to the vibrational energy of this bond. Therefore, in an SP the vibrations of the weakened and elongated $C_{spiro}-O$ bond may be excited the most intensely, assisting its final heterolytic cleavage.

c) Effect of structure of SPs in the ground and excited states on their photochemical properties

Let us compare the features identified in the structure of SPs in the ground state and the nature of the structural changes in the excited state with their photochemical activity. Unfortunately, there is no information in the literature on the quantum yields of photocleavage of a bond (ν) while the quantum yields of photocoloration φ_{AB}[44] represent the efficiency of photolytic conversion without taking into account the reverse formation of the closed form of an SP (from the *cis*-cisoid isomer) directly after bond cleavage. It is evident that in general the relationship $\varphi_{AB} \leqslant \nu$ is always true.

The photochemical properties of SP(I)–SP(IV) are described in detail in the literature.[44] The greatest length of the $C_{spiro}-O$ bond in the ground state, the length of which agrees within the limits of error in these SPs, has been established for these compounds. The nature of the subsequent change in length of this bond in the excited state of SP(I)–SP(IV) differs considerably. Charge transfer from the O atom to the NO_2 group will depend on the position of the NO_2 group in the benzene ring relative to the O(1) oxygen atom. The greatest transfer of charge will occur in an SP with these atoms at the *para*-position. Therefore in SP(I) and SP(IV) the $C_{spiro}-O$ bond in the excited state will be weaker and longer than in SP(II) and SP(III), which have the NO_2 group at the *ortho*-position. In accordance with this, the quantum yields of photocoloration for SP(IV) and SP(I) (0.60 and 0.45 respectively) are higher than for SP(II) and SP(III) (0.13 and 0.05).[29] Introduction of Br and Cl atoms into the benzopyran residue of the SP leads to additional ICT

from these atoms on to the π-system of the benzene ring as a result of mesomeric effects, which reduces ICT from the O atom. Moreover, Cl and Br, being heavy atoms increase the efficiency of intersystem crossing and radiationless deactivation of triplet states. Consequently, the quantum yields of the photolytic reaction of SP(I) and SP(III) are lower than for SP(IV) and SP(II) respectively.

As has already been mentioned, the $C_{spiro}-O$ bond in SP(V) in both the ground and excited states is elongated and weakened to a lesser degree than in SP(IV), and the quantum yield of photocoloration for SP(V)[47] is lower than for SP(IV). Nevertheless, this value for SP(V) is still fairly high (0.3). Kholmanskii et al.[47] believe that the high quantum yield of photocoloration of SP(IV) is due to an exchange interaction between an unpaired electron formed in the excited state on the N(1′) atom and the electrons of the σ-orbital of the $C_{spiro}-O$ bond. This type of interaction may assist cleavage of the $C_{spiro}-O$ bond.

The *cis*-cisoid isomer formed directly after cleavage of the $C_{spiro}-O$ bond in an SP is unstable and can readily revert to the initial form. In SP(I)–SP(V) the NO_2 group evidently plays a significant role in the stabilisation of the resulting intermediate. This group is known[49] to have amphi-electronic (π-acceptor and π-donor) properties depending on the electronic nature of the molecular residue of which it forms a part. In electron-rich systems the NO_2 group exhibits π-acceptor properties while in electron-deficient systems it has π-donating properties. Therefore, the NO_2 group will stabilise the open form of SP(I)–SP(IV) through delocalisation of the negative charge from the oxygen atom and formation of a quinoid structure (as was shown by Aldoshin et al.),[14] while the open form of SP(V) will be stabilised through donation of electron density to the cationic indoline part of the molecule.

Unfortunately, no information exists on the structure of unsubstituted SP. Using the arguments developed above, it may be assumed that the length of the $C_{spiro}-O$ bond in it should be intermediate between the length of this bond in SP(IV) and SP(V) and hence the quantum yield for cleavage of this bond should be high. However, the *cis*-cisoid intermediate formed by cleavage of this bond must be extremely unstable and there is a high probability that it would be converted to the initial closed form, which would significantly reduce the quantum yield of photolytic conversion of unsubstituted SP. In fact, quantum-chemical calculations on unsubstituted chromenes[46] showed that on the potential energy surface of the excited state there is no energy minimum that corresponds to a *cis*-cisoid structure.

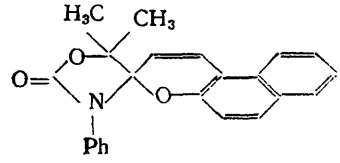
Thus, cleavage of the $C_{spiro}-O$ bond in the excited state may to a large extent be due to the further weakening and elongation of this bond during photoexcitation resulting from the same structural factors which caused the elongation and weakening of this bond in the ground state. Therefore, elongation of the $C_{spiro}-O$ bond in the ground state may serve as one of the criteria for photochemical activity in these compounds.

d) Effect of the nature and position of the substituents in SP molecules on the length of the $C_{spiro}-O$ bond

The results of X-ray diffraction analysis showed that transferring the NO_2 group from the *para*- to the *ortho*-position and also the introduction of electronegative halogen atoms into these positions actually has no effect on the length of the $C_{spiro}-O$ bond (see Table 1). At the same time, introduction of EA substituents into the indoline residue of the SP should lead to an increase in delocalisation of the UEP of the N(1′) atom in the π-system of the indoline benzene ring and a decrease in efficiency of interaction of this UEP with the σ*-orbital of the $C_{spiro}-O$ bond.

Support for this is provided by the results of an X-ray diffraction study on 1,3′,3′-trimethyl-5′-nitrospiro(indoline-2,2′[2*H*-1]benzopyran) [SP(V)] with the NO_2 group at the 5′-position of the indoline residue[24] (Table 1). In SP(V) the indoline and benzopyran parts of the molecule are also at right angles to each other. The benzopyran residue is virtually planar, as in SP(I)–SP(IV), and has the conformation of an envelope with dihedral angle along the line of N(1′)...C(3′) of 27.2°. The unshared electron pair of the N(1′) atom and the $C_{spiro}-O$ bond are at an angle of 168.8° while the π-UEP of the O atom and the $C_{spiro}-N(1')$ bond are at an angle of 145.2°. Introduction of the NO_2 group into the indoline residue at the *para*-position relative to the N(1′) atom leads to a contraction of the N(1′)–C(Ph) bond to 1.380(2) Å compared to the length of this bond [1.393(4)–1.413(5) Å] in SP(I)–SP(IV), SP(VIII), and SP(XI). The length of the N(1′)–C(Ph) bond in SP(I)–SP(IV), SP(VIII), and SP(XI) is similar to the length of the corresponding bond [1.413(3) Å] with a considerable contribution of the UEP of the N atom to the π-system of a neighbouring carbonyl group.[50] The lengths of the N(1′)–C(Ph) and (Ph)C–N(NO_2) bonds [1.380(2) and 1.461(2) Å] respectively] in SP(V) are similar to the corresponding bond lengths in *p*-nitroaniline [1.371(4)–1.380(5) Å and 1.450(5)–1.460(5) Å),[51,52] which is an indication of the increase in conjugation of the UEP of the N(1′) atom in SP(V) with the π-system of the benzene ring. As a result of this, the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction decreases and the $C_{spiro}-N(1')$ bond only decreases in length to 1.453(2) Å and the $C_{spiro}-O$ bond is only extended to 1.452(2) Å.

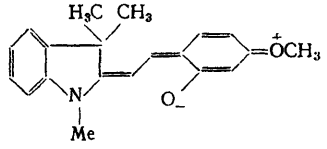
Confirmation of the effect of the electronic state of the N atom on the length of the $C_{spiro}-O$ bond is provided by the results of X-ray diffraction studies on SP(XXIII)[53] (SPs of this class are examined later in Section V). In SP(XXIII), as a result of the amide conjugation of the UEP of the N atom with the π-electron system of the carbonyl group, the activity of the UEP and efficiency of $n-\sigma^*$ interaction must be even lower than in SP(V). Therefore the $C_{spiro}-N$ bond (1.47 Å) becomes hardly any shorter while the $C_{spiro}-O$ bond (1.44 Å) is much less elongated than in SP(V).



SP(XXIII)

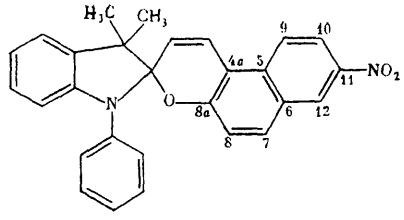
It is not possible to obtain crystals of unsubstituted SP that are suitable for X-ray diffraction analysis. The SP(VI) molecule appears to have a structure which is closest to that of unsubstituted SP.[29] The CH_3O group is known[54] to have very weak EA properties regardless of its position in the benzene ring. This group exhibits strong electron-donating (ED) properties when it is at the *ortho*- and *para*-positions of a benzene group. Thus, a CH_3O group at the 7-position of the benzopyran residue should have a weak effect on the electronic configuration of this residue and the molecular structure of 1,3′,3′-trimethyl-7-methoxyspiro(indoline-2,2′-[2*H*-1]benzopyran) (VI: $R' = CH_3$, $R^7 = OCH_3$) should be similar to the structure of unsubstituted SP.

The main structural parameters of SP(VI) are given in Table 1. The structure of the SP(VI) molecule is similar to the structure of SP(II), SP(III), and SP(IV*a*). The C(7)–O(2) bond of the methoxy group is bent by 15.6° from the plane of the phenyl residue. The length of the C_{spiro}–O bond [1.471(3) Å] is intermediate between the lengths of the same bonds in SP(I)–SP(IV) [1.485(4)–1.496(4) Å] and in SP(V) [1.452(2) Å]. Thus, even if the 7-OCH_3 group is able to exert a weak ED effect on the benzopyran fragment of the SP, the C_{spiro}–O bond in unsubstituted SP will be weakened and elongated not less than in SP(VI). However, in contrast to unsubstituted SP, the 7-CH_3O group in SP(VI) stabilises the resulting MC form, being involved in conjugation as shown in the diagram



Therefore SP(VI) in solution and even in the solid state becomes coloured on irradiation with UV-light.[55]

An X-ray diffraction study was carried out[28] on 1′-phenyl-3′,3′-dimethyl-11-nitrospiro(indoline-2,2′-[2*H*-1]naphthopyran) [SP(VII)], which contains an additional benzene ring annelated at the 5- and 6-positions.



SP(VII)

The main structural parameters of SP(VII) are given in Table 1. SP(VII) has a structure which is similar to that of SP(II), but annelation of the additional benzene ring and transfer of the NO_2 substituent to the 11-position lead to a contraction of the C_{spiro}–O bond to 1.460(2) Å compared to the length of this bond [1.492(3) Å] in SP(II). Although the C_{spiro}–O bond is still longer than a normal C–O bond,[15–17] its shorter length in SP(VII) compared to SP(II) indicates that there is a weakening of the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction in this molecule. As the geometric configuration of the UEP of the N(1′) and O atoms and C_{spiro}–O and C_{spiro}–N(1′) bonds in SP(II) and SP(VII) is the same (Table 1), the decrease in $n-\sigma^*$ interaction in SP(VII) may be due to a change in the electronic state of the O(1) atom in the spiro centre. In fact, the O(1)–C(8*a*) bond in SP(VII) is longer [1.372(3) Å] than that in SP(II) [1.356(3) Å]. This suggests that there is decrease in conjugation of the π-system of the naphthalene residue with the π-UEP of the O(1) atom, leading to a reduction in polarity of the C_{spiro}–O(1) bond and a weakening of the $n-\sigma^*$ interaction. This is also supported by the contraction of the C(22′)–N(1′) bond to only 1.450(3) Å, whereas in SP(II) this bond decreases to 1.432(3) Å.

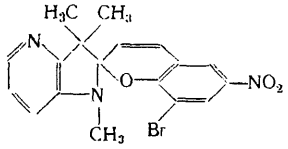
Thus, the presence of an additional benzene ring at the 5,6-position of the benzopyran residue and the transfer of the NO_2 group to the 11-position cause some contraction and strengthening of the C_{spiro}–O bond in SP(VII) compared to SP(I)–SP(VI), which in turn leads to a decrease in photochemical activity of naphthospiropyrans (NSPs).

Particular attention should be given to the fact that the quantum yield for photolytic conversion of an NSP, in contrast to SP(I), SP(III), and SP(IV), has proved very sensitive to the nature of the R′ substituent on the N(1′) atom. While replacement of R′ = CH_3 by R′ = Ph in spiropyrans has no effect on the quantum yield of photolytic conversion,[44,56] in NSPs the same change leads to a sharp fall in the value of φ—from 0.6 (R′ = Me) to 0.08 (R′ = Ph) in SP(VII).[57]

A structural analysis of the series SP(I), SP(IV)–SP(VI), SP(IX), and SP(XI) with R′ = CH_3 shows that the N(1′) atom in all of these compounds has the same pyramidal coordination and projects from the plane of the atoms bonded to it by 0.24–0.28 Å. Replacement of the CH_3 group on the N(1′) atom by the more bulky benzyl group, i.e. going from SP(IV) to SP(VIII), leads to an increase in the height of the pyramid to 0.34 Å but in other respects has no effect on the structure of the SP(VIII) molecule[25] (Table 1). Replacement of a CH_3 group by a C_6H_5 group makes it possible to conjugate the UEP of the N(1′) atom with the π-system of the benzene ring, the efficiency of which will be determined by the degree of coplanarity of the Ph-ring with the coordination plane of the N(1′) atom. In SP(II) and SP(VII), with values of the dihedral angle between these planes equal to 43.9 and 34.8° respectively, the N(1′) atom only projects from the plane of the three atoms bonded to it by 0.13 and 0.12 Å respectively, the UEP of the N(1′) atom conjugates with the π-system of the Ph substituent, and the activity of the UEP of N(1′) will therefore decrease. The fall in the quantum yield for photolytic conversion of SP(VII) may be related to weakening of the $n[N(1')]-\sigma^*(C_{spiro}-O)$ interaction. The dihedral angle between the plane of the Ph ring and the coordination plane of the N(1′) atom in SP(III) is 80° and N(1′) atom projects from the C(22′)C(7*a*)C(Ph) plane by 0.21 Å. Unfortunately, there are no data on the quantum yield for photolytic conversion of an SP(II) derivative with R′ = CH_3 and it was not possible to conduct an X-ray diffraction analysis of SP(III) and SP(VII) with R′ = CH_3 and SP(I) and SP(IV) with R′ = C_6H_5 because of the poor quality of the crystals, so the very interesting and important question concerning the effect of the degree of conjugation of the UEP of the N(1′) atom with a C_6H_5 residue on the quantum yield of photolytic conversion of SPs has no clear answer for the time being.

The synthesis of new photochromic SPs based on 4-azaindole has been reported.[58] The SPs obtained readily dissolve in polar and nonpolar solvents and some of them even in water. The small bathochromic shift of the long-wavelength absorption band of these compounds is due, in the opinion of Maisuradze et al.,[58] to the increase in EA properties of the pyridine ring in comparison to a benzene ring. The photosensitivity of azaindoline SPs towards UV radiation proved to be no lower and in some cases even higher than the photosensitivity of their indoline analogues.

The X-ray structural analysis of 1,3′,3′-trimethyl-6-nitro-8-bromospiro(4-azaindoline-2,2′-[2*H*-1]benzopyran) [SP(IX)] has been carried out.[27]



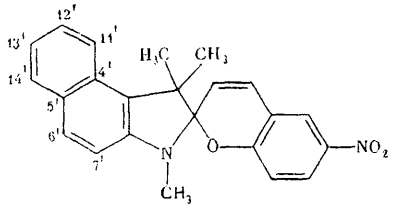
SP(IX)

The main structural parameters of SP(IX) are given in Table 1. Since the pyridine ring has stronger EA properties than the benzene ring, the length of the N(1′)–C(7*a*′) bond [1.386(6) Å] has a

tendency to decrease and although within the limits of experimental error it matches the length of this bond in SP(I) [1.398(5) Å] and in SP(V) [1.380(2) Å], it is shorter than in SP(II)–SP(IV) and SP(VI)–SP(VIII) [1.394(3)–1.416(4) Å]. These results indicate that there is some increase in conjugation of the UEP of the N(1′) atom with the π-system of the pyridine ring. However, the $C_{spiro}-O(1)$ bond [1.486(6) Å] in SP(IX), as in SP(I) [1.496(4) Å], is still elongated, which is an indication of strong $n[N(1')]-\sigma^*[(C_{spiro}-O(1)]$ interactions in the SP(IX) molecule. Moreover, in SP(IX), in contrast to the SP(I), the benzopyran ring is virtually planar and the π-UEP of the O(1) atom makes an angle of only 139.6° with the $C_{spiro}-N(1')$ bond rather than 160.2° as in SP(I). Therefore the $n[O(1)]-\sigma^*[C_{spiro}-N(1')]$ interaction in SP(IX) will be weaker than in SP(I). This is suggested by the greater contraction of the $C_{spiro}-N(1')$bond in SP(IX)—to 1.434(7) Å compared with 1.453(4) Å in SP(I).

Thus, in SPs based on 4-azaindole, just as in their indoline analogues, $n[N(1')]-\sigma^*(C_{spiro}-O)$ orbital interactions remain strong and the $C_{spiro}-O$ bond is elongated.

As has already been mentioned above, the quantum yield of photocleavage of the $C_{spiro}-$bond in SPs in many respects depends on the length of this bond in the ground state and the degree of ICT from the oxygen atom of the pyran ring to the benzene ring in the excited state, affecting a further weakening and stretching of the $C_{spiro}-O$ bond. In order to distinguish the influence of these factors, it is necessary to study SPs whose molecules would have the same structure in the ground state but a different pattern of electronic transitions in the excited state. The subject chosen for such a study was 1′,3′,3′-trimethyl-4′,5′-benzo-6-nitrospiro(indoline-2,2′-[2*H*-1]benzopyran [SP(X)].[26] It was assumed that annelation of an additional ring at the 4′- and 5′-positions of the indoline residue would have no substantial effect on the structure of the spiro centre



SP(X)

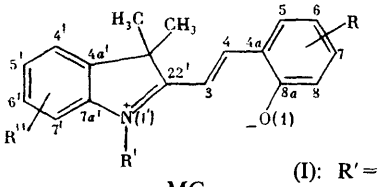
in SP(X) relative to SP(IV), but as had been shown in two studies[8,56] would lead to intramolecular energy transfer (IET) from the pyran heterocycle to the indoline system and would lower the efficiency of photocoloration of SP(X) compared to SP(IV).

The main structural parameters of SP(X) are given in Table 1. Spiropyrans (X) and (IV) have the same structure. The benzopyran residue in SP(X) is virtually planar, as in the SP(IV*a*) molecule. The $C_{spiro}-O(1)$ bond is extended to 1.478(7) Å and within the limits of experimental error it matches the average length of this bond in SP(IV) [1.486(4) Å]. Since annelation of the benzene ring at the 4′- and 5′-positions of the indoline residue does not affect the structure of the spiro centre in the SP(X) molecule, which has the same characteristics as in SP(IV), the decrease in the quantum yield for photolytic conversion of SP(X) to 0.026, compared to 0.60 for SP(IV),[56] is evidently due solely to radiationless deactivation processes in the excited state, in particular with ICT from the pyran to the indoline ring. With such a transfer of energy, ICT from the O(1) oxygen atom to the benzene ring and the nitro group of the benzopyran residue is substantially reduced. Therefore it may be assumed that in the excited state the interaction between the UEP of the N(1′) atom and the σ*-orbital of the $C_{spiro}-O(1)$ bond will be weaker in SP(X) than in SP(IV), and although the C(22′)–O(1) bond in SP(X) is elongated and weakened in the ground state it will undergo cleavage with greater difficulty.

Another factor which has a considerable effect on the efficiency of the photochemical conversion of SPs is a process which competes with the photoreaction, namely, the radiationless deactivation of excited states through internal conversion and intersystem crossing. It is known[59] that the presence of heavy atoms substantially increases the rate of all "singlet⟷triplet" processes, and therefore heavy atoms are effective quenchers of excited states. It has already been noted in Section II.2c that the introduction of heavy Cl and Br atoms into the 6- and 8-positions of the benzopyran residue does not have any substantial effect on the structure of the SP but reduces the quantum yield of photoconversion of these compounds. This type of influence from heavy atoms in the benzopyran residue may be due either to the effect of heavy atoms increasing the radiationless deactivation of excited states or to the mesomeric donor effect of these atoms decreasing ICT from the oxygen atom to the phenyl residue. In order to study the role of heavy atoms in SP molecules, X-ray diffraction analysis was conducted on 1,3′,3′-trimethyl-4-chloro-6-nitrospiro(indoline-2,2′-[2*H*-1]benzopyran [SP(XI)],[30] which contains a Cl atom at the 4-position of the benzopyran residue. The Cl atom at the 4-position of the pyran ring does not have any marked effect on the geometry of the molecule and the distribution of bond lengths in it. The SP(XI) molecule has a structure which is the same as that of SP(IV). As in SP(IVa), the benzopyran part of the molecule in SP(XI) is virtually planar. The C(22′)–N(1′) bond length of 1.438(2) Å and C(22′)–O(1) bond length of 1.479(2) Å within the limits of experimental error match the values of these bond lengths in SP(IV) (see Table 1). Nevertheless, the photochemical activity of SP(XI) proves to be considerably lower than the photochemical activity of SP(IV). In the excited state the Cl atom at the 4-position also should not affect ICT from the O atom to the benzene ring. Therefore, the reduction in photochemical activity of SP(XI) is apparently due solely to the effect of the Cl atom as a heavy atom.

III. The structure of open merocyanine forms of indoline spiropyrans

Since one of the important characteristics of photochromic systems based on SPs is the lifetime of the open merocyanine forms of SPs, it is necessary to carry out a detailed study of the structure of MCs and to identify the structural factors which stabilise SPs in the open state. The structure of different MCs and the energy of their intermolecular interactions in crystals, and the thermodynamic and kinetic stability of the isomers identified will then be examined.



MC

(I): $R'=CH_3$, $R^6=NO_2$, $R^8=Br$;
(II): $R'=C_5H_{11}$, $R^6=NO_2$, $R^8=Br$;
(III), (IV): $R'=p\text{-}CH_3C_6H_4$, $R^6=NO_2$, $R^8=NO_2$, $R''=CH_3$;
(V): $R'=H$, $R^6=NO_2$, $R^8=NO_2$.

1. Molecular structure of merocyanines

In crystals of MC(I) the bipolar structure (A) appears to be stabilised to a considerable extent through solvation of the negatively charged O(1) oxygen atom by a water molecule (Fig. 2), which may substantially affect the electronic structure and stability of the MC molecule.

The crystalline structure of solvates of MC(I) provides a basis for the assumption that replacement of a methyl group on the N(1′) atom in the indoline ring by a more bulky group can inhibit solvation of the phenolate oxygen atom. In order to confirm this hypothesis, an X-ray diffraction study was carried out on the pentyl-substituted MC(II), in which the pentyl substituent on the N(1′) atom is similar to the methyl group in terms of its electronic properties.[60,61] The MC(II) molecule does not form solvates in the crystalline state. Just as in MC(I) crystals, MC(II) molecules (Fig. 6) have an almost planar *trans*-cisoid structure. The slight deviation from planarity manifests itself in twists about the C(22′)–C(3), C(3)–C(4), and C(4)–C(4*a*) bonds of 5.5, 6.7, and 8.6° respectively.

The distribution of bond lengths in the MC(II) molecule is in general terms similar to the distribution of bond lengths in the MC(I) molecule. However, the absence of solvate water molecules in MC(II) crystals leads to some redistribution of electron density in the MC(II) molecule. Thus, the length of the O(1)–C(8*a*) bond is reduced to 1.228(6) Å, which corresponds to the length of a C=O double bond.[15] Contraction of the O(1)–C(8*a*) bond in MC(II) is accompanied by a further decrease in bond angle of C(4*a*)C(8*a*)C(8) to 112.8(1)°, which is an indication of the increasing importance of σ-electron repulsion from the O(1) atom. The C(4*a*)–C(8*a*) and C(8a)–C(8) bonds are extended even more and the C(7)–C(8) bond is shorter in comparison with the lengths of these bonds in MC(I). As in the MC(I) molecule, the N(2)–C(6) bond [1.437(6) Å] is considerably shorter than this bond in the closed form,[14] the O(2)N(2)O(3) angle [121.5(5)°] being even smaller than the "equilibrium" value. This type of structure for the *p*-nitrophenolate residue suggests that there is a greater contribution of the resonance quinoid form (B) (see Fig. 3) to the zwitterion structure (A) of unsolvated MC(II) molecules compared to solvated MC(I) molecules. As in MC(I), the contribution of the canonical form (C) is appreciable in MC(II) molecules (see Fig. 3). The N(1′)–C(22′) bond in MC(II) [1.316(5) Å] is even shorter than in MC(I), which is an indication of its complete double bond character and that the positive charge is mainly located on the N(1′) atom.

Thus, the research carried out indicated that the structure of open forms of SPs can be represented by resonance forms (A) (the greatest contribution), (B), and (C), with the contribution of each of these forms varying in accordance with the nature of the substituents in the molecule. Stabilisation of open MC molecules must be related to the stabilisation of one of these resonance structures. The structure of MC(I) crystals suggests that solvation of the O(1) phenolate atom stabilises the zwitterion structure directly to a greater extent. Stabilisation of the canonical structure (C) can be achieved,

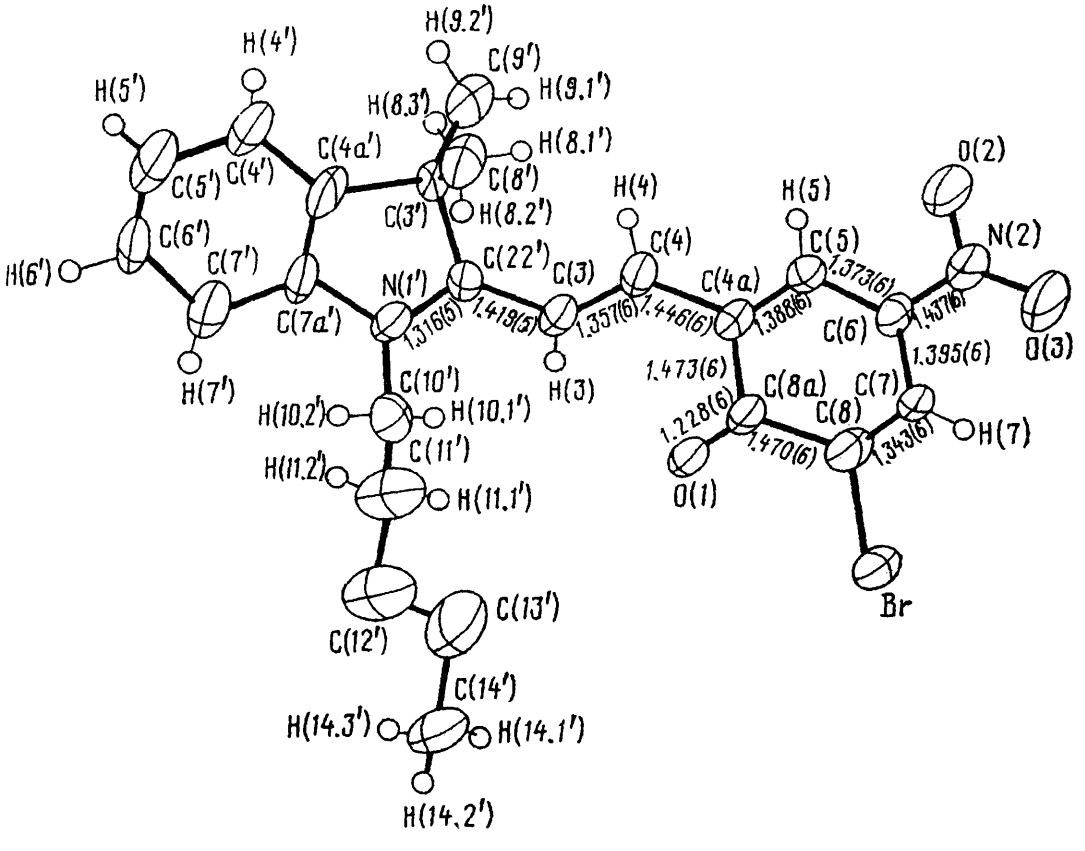
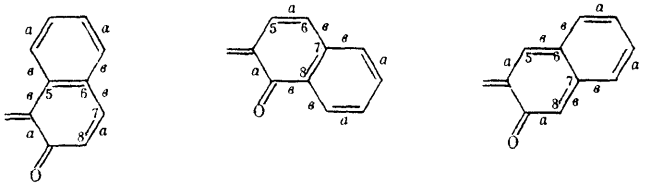


Figure 6. General shape of the MC(II) molecule.

for example, through annelation of additional benzene rings to the phenolate ring. At the same time annelation of additional benzene rings at the 5,6- and 7,8-positions will further stabilise form (C) because of the preservation of aromaticity and specificity of structure of a naphthalene residue with shortened "*a*" bonds and elongated "*b*" bonds, while annelation at the 6,7-position will lead to its destabilisation.



In MC(I) and MC(II) *p*-NO_2 substituents in the phenolate ring displace the equilibrium towards the quinoid form (B) and hence stabilise the unstable zwitterion form. It was suggested[61] that introduction of an additional NO_2 group into the *ortho*-position relative to the O(1) atom of this residue should increase the stability of the open MC form. X-Ray diffraction analysis of such a merocyanine, MC(III), showed that this compound crystallises in two polymorphic forms—monoclinic and rhombic.

In the monoclinic form MC(III) molecules have a nearly planar *trans*-structure (Fig. 7) with slight deflections about the C(22′)–C(3), C(3)–C(4), and C(4)–C(4*a*) bonds of 3.1, 4.7, and 2.7° respectively, which is similar to the structure of MC(I) and MC(II). However, in contrast to MC(I) and MC(II), the phenolate oxygen atom in MC(III) in almost equal probability occupies the *S-cis*- or *S-trans*-positions relative to the C(4)–C(4*a*) bond. Thus, the *trans*-cisoid isomer and *trans*-transoid isomer, which has been detected experimentally for the first time, occur in equal ratios in the crystalline state.

The *trans*-transoid isomer, which constitutes ~50% of a crystal, is solvated by a water molecule [O(1′)...O(H_2O) distance is 2.44 Å], which also occupies ~50% of the independent positions. The hydrogen bond formed in the solvate is one of the shortest hydrogen bonds.[62] As a result of the phenolate residue being randomly oriented in two positions, the distribution of bond lengths in it is averaged out and it is not possible to make any conclusion about the nature of the redistribution of bond lengths on introducing a second NO_2 group into the *ortho*-position relative to the O(1) atom. However, the C(6)–N(3) and C(8)–N(2) bond lengths with both nitro groups are shortened (see Fig. 7) and the O(2)N(2)O(3) and O(4)N(3)O(5) angles [121.3(6) and 120.0(6)°] are smaller than the "equilibrium" values. This suggests that there is a strong resonance interaction between these groups and the π-system of the benzene ring. The C(4*a*)–C(5) and C(4*a*)–C(8*a*) bonds are elongated while the C(6)–C(7) and C(7)–C(8) bonds are shortened (see Fig. 7) in comparison with the normal value of a bond length in a benzene ring. The remaining bond lengths in the MC(III) molecule within the limits of experimental error match the bond lengths in the MC(I) and MC(II) molecules, although the N(1′)–C(22′), C(22′)–C(3), and C(3)–C(4) bonds are somewhat longer.

X-Ray structural analysis of the rhombic form [MC(IV)] showed[61] that the two isomers—*trans*-cisoid and *trans*-transoid—also occur in crystals of this polymorph in nearly equal proportions. The pattern of distribution of bond lengths in MC(IV) within the limits of experimental error is in line with the distribution of bond lengths in MC(III).

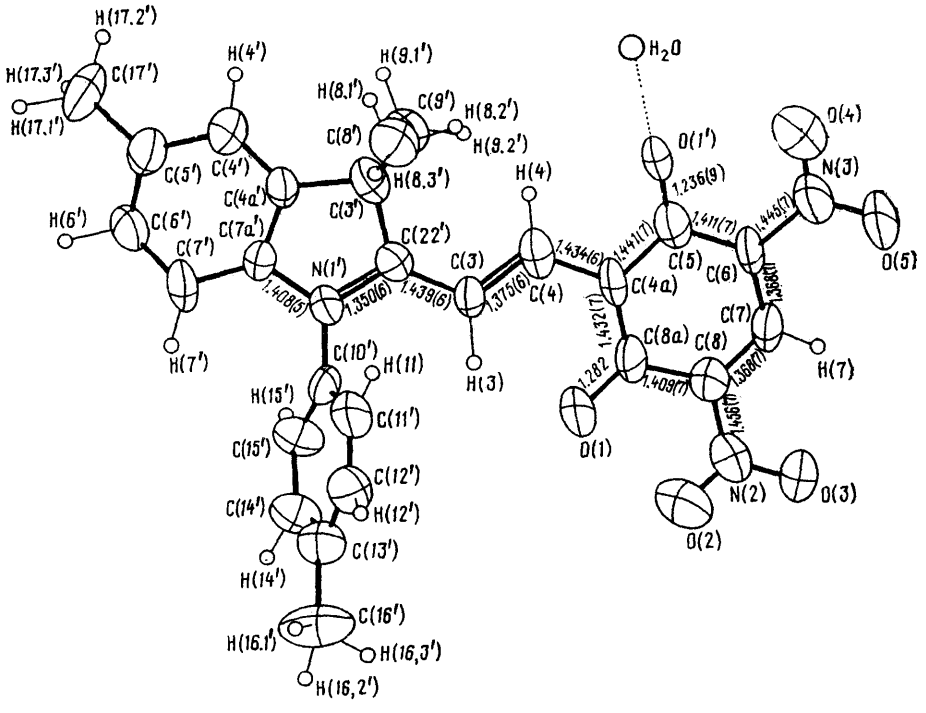


Figure 7. General shape of the MC(III) molecule.

Crystals of MC(IV), like crystals of MC(III), contain solvate water molecules which occupy ~50% of the independent positions. However, in contrast to MC(III), it is the sterically less accessible O(1) atom of the *trans*-cisoid isomer that is solvated [O(1)...O_{H_2O} distance is 2.97(3) Å] rather than the O(1) atom of the *trans*-transoid isomer, which causes the phenyl substituent on the N(1′) atom to deviate from the plane of the molecule by 87.9°. In crystals of MC(IV) there are also other water molecules that do not solvate the MC molecules, and they occupy about 25% of the independent positions and are situated at an O...O distance of 2.30 Å from the solvating water molecules.

Thus, solvation of the phenolate O atom is evidently typical for MC molecules in polar solvents if steric factors do not prevent this.

The introduction of an additional NO_2 group into the phenolate residue stabilises a further isomer—the *trans*-transoid form—which evidently exists in solution in equilibrium with the *trans*-cisoid isomer, resulting in their co-crystallisation. This conclusion made it necessary to conduct a more detailed study of the structure of the *trans*-transoid isomer. An X-ray diffraction study was carried out on the *o,p*-dinitro-substituted MC(V), in which the hydrogen atom of the vinyl group is replaced by a CH_3 group, which must inhibit the formation of the *trans*-cisoid isomer. In fact, in crystals of MC(V) the molecules have a *trans*-transoid structure (Fig. 8) and are linked together in a chain via a strong O(1)...$H_{N(1')}$ hydrogen bond [1.70(4) Å]. The steric interactions which occur between the atoms of the methyl group of C(10) and the *syn* H(5) atoms "eject" the phenolate residue from the plane of the molecule by a turn of 20.3° about the C(4)–C(4*a*) bond. However, this turn is evidently not sufficient to reduce the steric strain in the molecule, and the tendency to retain a planar structure with delocalised electron density prevents a further loss of planarity by the molecule, resulting in the C(4)C(3)C(10) bond angle being distorted to 124.6(4)° and the C(3)C(4)C(4*a*) and C(4)C(4*a*)C(5) angles are even changed to 133.3(4) and 127.0(4)°. Twists of the groups about the C(22′)–C(3) and C(3)–C(4) bonds only amount to 6.1 and 8.3°. The O(1)–C(8*a*) bond length [1.269(5) Å] is similar to the length of this bond in the MC(I) molecule, where the O(1) atom, as in MC(V), particpates in the formation of a strong hydrogen bond. These bonds are longer than the O(1)–C(8*a*) bond in the MC(II) molecule, in which the O(1) atom does not participate in intermolecular hydrogen bonding. The size of the intramolecular bond angle of C(4*a*)C(8*a*)C(8) [115.4(5) Å] in MC(V) is also close to that for the same angle in MC(I), which suggests that there is the same σ-electron repulsion from the O(1) atoms in both molecules.

It was surprising to find that in MC(V) the C(6)–N(2) bond length [1.480(7) Å] within the limits of experimental error matches the lengths of the same bonds in closed SPs,[30] and is not shorter than them as in MC(I) and MC(II). The size of the O(2)N(2)O(3) bond angle [125.0(6)°] is close to the "equilibrium" value of this angle in aromatic nitro compounds.[18] All of this is an indication of the much weaker resonance interaction between the *p*-NO_2 group in MC(V) and the π-system of the phenolate residue than in MC(I) and MC(II). The length of the C(8)–N(3) bond [1.462(6) Å] is shorter than C(6)–N(2) although it is still longer than in MC(I) and MC(II). The O(4)N(3)O(5) bond angle [121.6(5)°] is also less than the "equilibrium" value. Since it was shown[18] that there is no correlation between the length of a C_{Ac}–N_{NO_2} bond and the angle of rotation of the NO_2 group about this bond, the results obtained suggest that there is a greater resonance interaction between the *o*-NO_2 group and the π-system of the benzene ring than for the *p*-NO_2 group. In the benzene ring two bonds—C(4*a*)–C(8*a*) and C(8*a*)–C(8)—are elongated while only the C(7)–C(8) bond is appreciably shortened (see Fig. 8). Taking into account this structure of the *o*,p-dinitrophenolate residue, such a distribution of

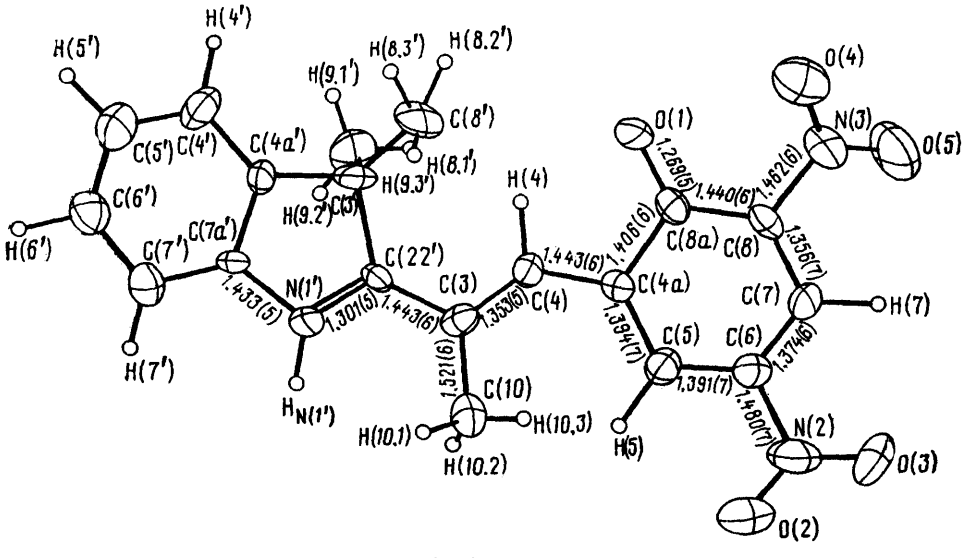
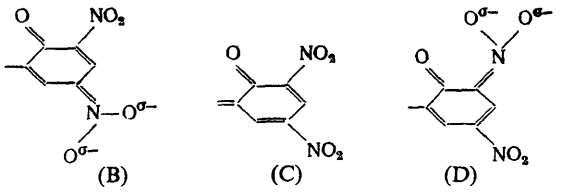


Figure 8. General shape of the MC(V) molecule.

the bond lengths in the phenolate ring is unlikely to result from the contribution of the resonance quinoid forms (B) and (D) but has more complex origins.

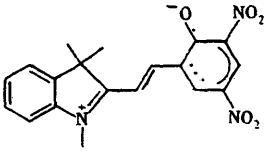


(B) (C) (D)

The contribution of the quinoid form (C) to the structure of the phenolate residue also appears to be small, and the increase in length of the C(22′)–C(3) bond to 1.443(6) Å and the further contraction of the N(1′)–C(22′) bond to 1.301(5) Å compared to the lengths of these bonds in MC(I) and MC(II) is an indication of the decrease in contribution of this form to the structure of the complete MC(V) molecule. The overall distribution of bond lengths in the phenolate residue may occur as a result of σ-electron repulsion from the negatively charged O(1) atom and the electron-acceptor effect of the NO_2 substituents. The latter conclusion is consistent with the statistical data of Holden and Dickinson,[18] according to which the bond lengths in the benzene ring adjoining a nitro group have a tendency to shorten.

It should be noted that despite the statistical disordering of the *o,p*-dinitro-substituted phenolate residue in MC(III) and MC(IV), the distribution of bond lengths in them is similar to that found in MC(V).

Thus, the MC(V) molecule with *o*- and *p*-NO_2 groups in the phenolate residue mainly has the bipolar structure (E) with appreciable disruption of aromaticity in the phenolate ring.



(E)

As was mentioned above, an important characteristic of an SP is the number of cycles for the photolytic conversion

$$SP \overset{h\nu}{\rightleftarrows} MC$$

without appreciable decomposition of the system. It is known[63] that SPs containing 8-OCH_3 and 6-NO_2 substituents in the benzopyran part of the molecule are more stable to decomposition. The structure of the merocyanine form of 1-hydroxyethyl-3,3′-dimethyl-6-nitro-8-methoxyspiro(indoline-2,2′-[2*H*-1]benzopyran [MC(VI)] (Fig. 9) has been studied.[64] In the crystalline state MC(VI) molecules are linked together through strong chains of hydrogen bonds of the type O(1)...$H_{O(4')}$ [1.78(3) Å] [O(1)...O(4′) = 2.64(1) Å], which results in elongation of the O(1)–C(8*a*) bond to 1.253(4) Å, which is typical for zwitterion molecules, in which the length of this bond is 1.26 Å. However, in other respects the distribution of bond lengths in MC(VI) differs substantially from

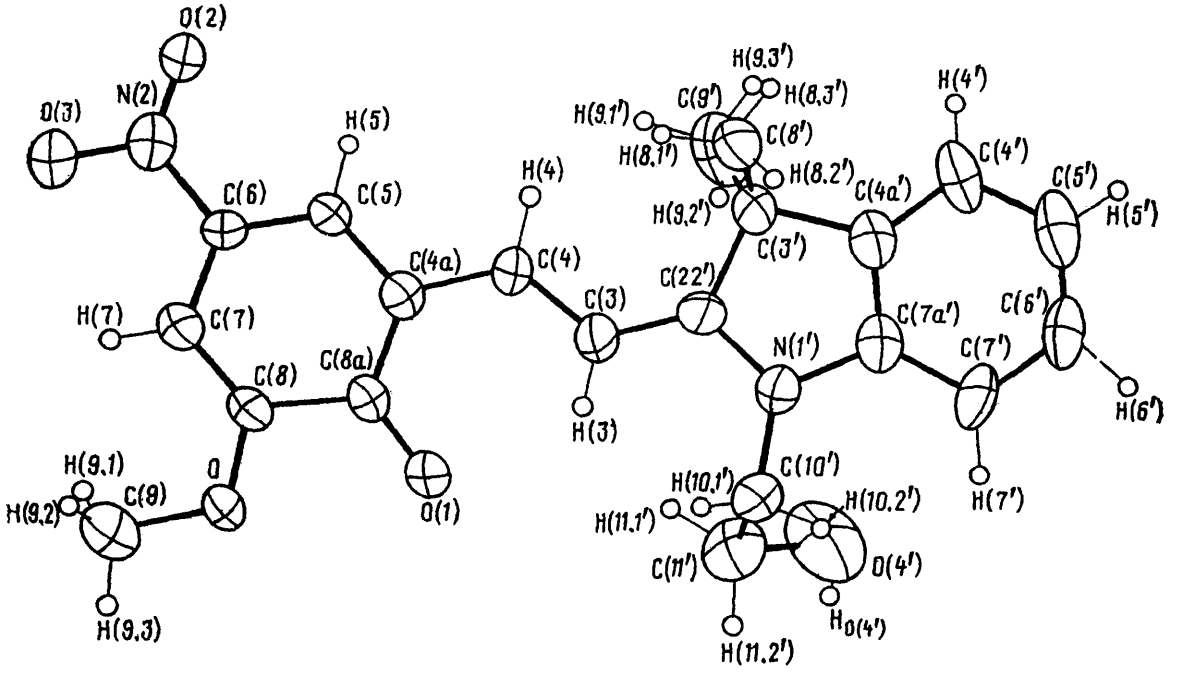


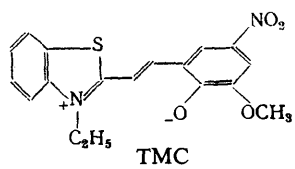
Figure 9. General shape of the MC(VI) molecule.

that in MC(I)–MC(V); the N(1′)–C(22) and C(3)–C(4) bonds [1.352(4) and 1.366(4) Å respectively] are elongated while the C(22′)–C(3) and C(4)–C(4*a*) bonds [1.403(4) and 1.444(4) Å] are shortened. This type of distribution of bond lengths in MC(VI) and at the same time the C(5)–C(6) and C(7)–C(8) bonds decreasing in length to 1.376(4) and 1.345(5) Å suggests that there is an increase in contribution of the quinoid form (C) (see Fig. 3) to the structure of MC(VI). The decrease in zwitterion character of the MC(VI) molecule and the greater contribution of the less reactive quinoid form to its structure may be responsible for the increase in stability of this system.

2. Geometric isomers of merocyanine forms

A study of the geometric isomerism and relative stability of the isomers of the open merocyanine forms is very important for an understanding of the mechanism of photochromism in SPs and to account for the spectroscopic behaviour of MCs, in particular the positions and occurrence of long-wavelength absorption, which together with the photoactivity of SPs and the stability of MCs constitute an important property which determines the practical application of SPs.[2,65] Many theoretical studies[46,66–68] have dealt with the question of the relative stability of the isomers of small model SPs and MCs and the effect of different substituents on their spectroscopic properties.

X-Ray diffraction analysis of MC(I)–MC(VI) showed that only the planar *trans*-cisoid and *trans*-transoid isomers exist in the crystalline state. The first of these occurs in crystals of MC(I)–MC(IV), MC(VI), and the open form of a benzothiazole SP–(TMC)—as studied by Miler-Strenger et al.,[69] while the second occurs together with the *trans*-cisoid isomer in crystals of MC(III) and MC(IV), whose molecules contain two nitro substituents in the phenolate residue.



TMC

It was concluded from the results of quantum-chemical calculations[61] that the *trans*-cisoid and *trans*-transoid isomers of MCs are similar in energy. In MCs with a single nitro group in the phenolate residue there is a substantial transition barrier between them, but introduction of two nitro substituents into the *ortho*- and *para*-positions of the phenolate residue lowers this barrier to such an extent that these isomers can readily undergo interconversion in solution. In fact, co-crystallisation of both isomers of the *o,p*-dinitro-substituted MC(III) and MC(IV) may also indicate that the packing energy of these isomers is virtually the same and in solution they occur in approximately equal concentrations.

The lowering of the rotation barrier about the C(4)–C(4*a*) bond when two electron-acceptor nitro groups are introduced into the phenolate residue is evidently related to the increased contribution of form (E) to the structure of this type of molecule, reducing the $\pi-\pi$ interaction between this residue and the remaining part of the molecule.

The results obtained cast doubt on the theory that the complex nature of the absorption spectrum of open merocyanine forms of SPs is due to the presence of four different stereoisomers in the solid state and in solution.[70,71] Furthermore, calculations on the absorption spectra of model isomers of 2*H*-chromenes show that these isomers are indistinguishable in the region of long-wavelength absorption.[66] In several studies[72–76] the suggestion that coloured and colourless forms of SPs are associated has been made in order to account for the spectroscopic properties of MCs. The similarity of the absorption spectra of MCs in nonpolar solvents (at low temperatures), in an amorphous state, and in thin homogeneous crystalline films suggests that the coloured form of SPs in the liquid and solid states has the same structure. Hence there is definite interest in the packing of MC molecules and energy of intermolecular interaction in crystals.

3. Nature of the molecular packing and energy of intermolecular interactions in merocyanine crystals

Since this question has been discussed by us in detail in a review article,[61] we shall only report here the main results and conclusions of this study.

The crystalline structure of open merocyanine forms of SPs is an indication of the well-defined tendency of MC molecules to form different aggregates. This is due to the planar structure and high polarity of MC molecules, and consequently, in addition to van der Waals forces, electrostatic and dipole–dipole interactions also play a significant role in the formation of aggregates. Calculations of the energy of crystalline MC structures show that the electrostatic interaction in the aggregates can amount to ~50% of the van der Waals interaction. The strongest aggregates are formed in MC(II) crystals, in which the molecules are arranged in stacks on top of each other according to the principle "head over tail". The pairing energy of the van der Waals and electrostatic interactions, without even taking account of the dipole–dipole interaction, in these stacks is approximately –26 kcal mol^{-1}. Solvated MC molecules form different aggregates through strong hydrogen bonds according to the principle "head to head" and "head to head, tail to tail".

Bulky alkyl substituents on the N(1′) atom can inhibit solvation of the *trans*-cisoid isomer of MCs, although they do not prevent the formation of "head to tail" aggregates. A methyl substituent on the N(1′) atom does not inhibit the solvation of *trans*-cisoid isomers of MCs. Solvation of a phenyl-substituted MC results in the phenyl substituent turning about 90° from the plane of the molecule and disrupting the conjugation of the UEP of the N(1′) atom with the π-system of the Ph residue, which is evidently balanced by the gain in energy from solvation of the molecule. Solvated molecules of *trans*-cisoid MC isomers form aggregates through hydrogen bonds with solvate molecules.

In the *trans*-transoid isomers the substituents on the N(1′) atom do not inhibit solvation. A solvated *trans*-transoid MC isomer can form both "head to tail" aggregates and aggregates with solvate molecules. In MC(I) crystals the aggregates comprise solvated MC molecules joined by a hydrogen bond. In these associates the molecules are arranged "head to head" at an angle of ~110° to each other, so the electrostatic attraction energy between them is reduced but the total energy of the van der Waals and electrostatic interactions is approximately –22 kcal mol^{-1}. In crystals of MC(V) the strongest aggregates (~–17 kcal mol^{-1}) are formed through the molecules being linked via hydrogen bonds in chains and also through intermolecular interactions in parallel to the molecules arranged "head to head" in layers. In the crystalline structure of MC(VI) repeating chains in which the pairing energy of intermolecular interactions is –10 kcal mol^{-1} can be distinguished.

The formation of quite strong aggregates in crystals of MC(I)–MC(VI) with different types of packing provides a basis for

the assumption that these aggregates can also be preserved in solution. In crystals only the energetically most stable forms of molecular association and those most favourable for packing usually occur, and so in MC solutions these aggregates can be even more diverse. At the same time in nonpolar aprotic solvents, for MC molecules not bound through a specific intermolecular interaction with solvent molecules formation of "head to tail" aggregates is the most probable. In protic polar solvents, formation of solvates combined into different associates through hydrogen bonds is the most probable. The formation of solvates and aggregates is a further factor stabilising the highly polar merocyanine forms and a more probable cause of the complex absorption spectrum of MCs than the proposed existence of various isomers.

IV. Effect of the nature and relative orientation of the heteroatoms in the spiro centre on the structure and photochemical properties of spiropyrans

The considerable influence of specific $n-\sigma^*$ orbital interactions of the heteroatoms in the spiro centre of indoline SPs on the structure and photochemical properties of these compounds suggests that a change in the nature and relative orientation of the heteroatoms in the spiro centre can be an effective means of modifying the structure and obtaining new classes of photochromic SPs. Therefore in this section we shall examine the structure of SPs containing different heteroatoms in the spiro centre.

1. Structural features of indoline spirothiopyrans containing S and N heteroatoms in the spiro centre

Aldoshin et al.[77] carried out an X-ray diffraction study on 1′phenyl-3,3′-dimethyl-6-nitrospiro(indoline-2,2′-[2*H*-1]benzothiopyran) [SP(XII)] (Fig. 10).

Replacement of the oxygen atom in SP(IV) by a sulphur atom [SP(XII)] resulted in a reduction of photoconversion activity of the latter at 293 K ($\varphi \approx 0.1$) compared to that of SP(IV) ($\varphi = 0.76$)[44] in solutions of dimethylformamide and toluene. At 77 K in polystyrene and polymethyl methacrylate the photochemical activity of SP(XII) increases ($\varphi = 0.7$) whereas the photochemical activity of SP(IV) ($\varphi = 0.1$) decreases markedly under the same conditions.

This type of behavioural pattern of SP(XII) compared to SP(IV) becomes clear if its structure is analysed. In SP(XII), as in other photochemically active SPs, the C(22′)–S bond [1.866(2) Å] which is cleaved on photoexcitation is considerably longer than the corresponding bonds in six-membered heterocycles (1.80–1.83 Å).[16,17] The C(22′)–N(1′) bond [1.484(3) Å] in SP(XII), in contrast to that in SP(IV), is not shortened, and its length corresponds to the lengths of normal $C_{sp^3}-N$ bonds (1.47–1.48 Å) in five-membered heterocycles.[15] Therefore elongation of the $C_{spiro}-S$ bond in SP(XII) cannot be accounted for using the concept of $n-\sigma^*$ interactions in the spiro centre proposed for SPs.

Replacement of the oxygen atom at the spiro centre by a sulphur atom, which has an ionisation potential similar to that of the nitrogen atom,[78] evidently levels out the donating capacities of the UEP of the S and N atoms. Furthermore, the C(22′)SC(8*a*) bond

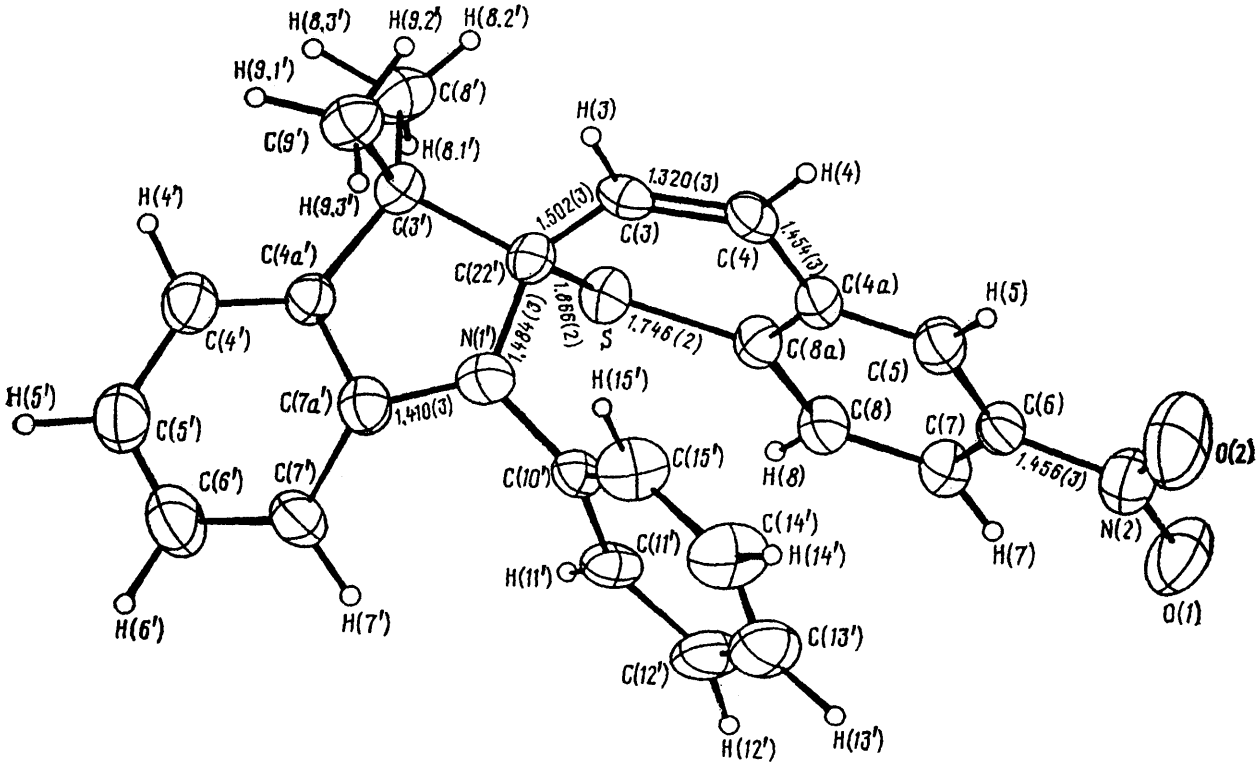


Figure 10. General shape of spirothiopyran SP(XII).

angle in SP(XII) proved to be 101.9°, whereas in SP(I)–SP(IX) the C(22′)O(1)C(8*a*) angles are in the range 120–124°. These findings could suggest that hybridisation of the S atom in SP(XII) is close to sp^3 while the O atom in SP(I)–SP(XI) is close to sp^2-hybridisation. With sp^3-hybridisation of the heteroatom there is a substantial decrease in conjugation of its UEP with the π-system of the benzene residue, hence the polarity of the C(22′)–S bond in SP(XII) will be much less than the polarity of the C(22′)–O bond in SP(I)–SP(XI) and the n[N(1′)]–σ*[C(22′)–S] interaction in SP(XII) will be weaker than the n[N(1′)]–σ*[C(22′)–O] interaction in SP(I)–SP(XI). Elongation of the C(22′)–S bond compared to the C(22′)–O bond in SP(I)–SP(XI) and the resulting withdrawal of the UEP of the S atom from the σ*-orbital of the C(22′)–N(1′) bond also reduces the n(S)–σ*[C(22′)–N(1′)] interaction, so in SP(XII) these n–σ* interactions are evidently small and balance each other.

The elongation of the C(22′)–S bond to 1.866(2) Å in SP(XII) has been attributed[77] to steric interactions between the *gem*-methyl groups and the heteroatom of the thiopyran ring. These interactions give rise to distortion of the indoline residue and its inflection along the line of C(3′)...N(1′) in the closed forms SP(I)–SP(XI), while in SP(XII), which contains the more bulky S atom compared to an O atom, the C_{spiro}–S bond is further elongated.

Because of the sp^3-hybridisation of the S atom and the weak overlap of its UEP with the π-system of the benzene ring, no significant positive charge develops on the S atom[18,56] during photoexcitation of the lowest electronic levels of the thiopyran residue in the SP(XII) molecule. Therefore, in contrast to SP(I)–SP(XI), in SP(XII) and in the excited state the n–σ* interactions will have no substantial effect on the length of the C_{spiro}–S bond and its cleavage. For this reason the mechanism of α-cleavage of this bond proves ineffective for SP(XII).[47] The observed photochemical properties of SP(XII) are evidently related to a vibrational mechanism for cleavage of the C_{spiro}–S bond, in which the electron excitation energy will be unequally converted into vibration energy of the weakest individual bonds.[48] In a spirothiopyran this is the C_{spiro}–S bond, whose vibrations should be excited more than the others. When there is steric hindrance between the S and C(8′) atoms, this results in cleavage of the C_{spiro}–S bond. Support for the decisive role of a vibrational mechanism of bond cleavage in spirothiopyrans is provided by the absence of any noticeable electronic effect from the 6-NO_2 group on their photochemical properties, in contrast to the SPs described by Betelson.[2]

Vibrational cleavage of the less polar C_{spiro}–S bond compared to C_{spiro}–O in spirothiopyrans can occur homolytically rather than heterolytically as in SP(I)–SP(IX). In contrast to SP(I)–SP(XI), the coloured form of SP(XII) is evidently not the most stable zwitterion structure but is only its thermodynamically unstable, intermediate isomer X.

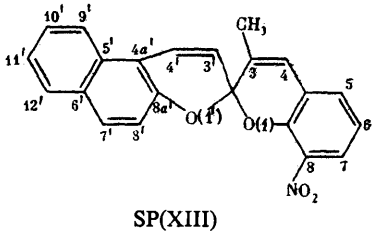
$$(A) \xrightarrow{h\nu} (A^*) \xrightarrow{\varphi_{breaking}} (X) \xrightarrow{\varphi_{colour}} (B)$$

When the temperature is lowered to 77 K this isomer (X) is stabilised and the quantum yield of the reaction increases. At 293 K in solution the reverse dark reaction (X)→(A) is efficient, and the quantum yield of reaction is low, although according to the results of flash photolysis the short-lived coloured form is formed in solution (in small quantities) even at 293 K.

2. Structure of "symmetrical" spiropyrans consisting of two benzopyran residues

It was demonstrated in IV.1 that the efficiency of orbital hyperconjugation in the spiro centre, which affects the photochemical properties of SPs to a considerable extent, depends both on the geometric configuration of the UEP of the heteroatom and the adjacent bonds and on the electronic properties of the heteroatoms. Since "symmetrical" spiropyrans contain the same heteroatoms in the spiro centre, their electronic properties and the efficiency of n–σ* interactions will mainly depend on the electronic state of the heteroatoms as determined by the nature and position of substituents in the benzopyran residue.

An X-ray study of SP(XIII) (Fig. 11) has been carried out.[79]



SP(XIII)

The orientation of the π-UEP of the O(1) and O(1′) atoms relative to the adjacent C(22′)–O(1′) and C(22′)–O(1) bonds in SP(XIII) is the same, with angles of 159.2 and 161.4° being formed respectively. Nevertheless, the bond lengths of C(22′)–O(1) [1.459(1) Å] and C(22′)–O(1′) [1.434(2) Å] in the spiro centre of SP(XIII) proved to be different. Introduction of the electron-withdrawing NO_2 group into the 8-position of SP(XIII) leads to a contraction of the O(1)–C(8*a*) bond to 1.358(2) Å, which, as in SP(II) and SP(III) where the lengths of these bonds are 1.356(3) Å, suggests that there is an increase in conjugation of the π-UEP of the O(1) atom with the π-system of the benzene ring.

Annelation of an additional benzene ring at the 5′, 6′-position of the benzopyran residue results in an elongation of the corresponding O(1′)–C(8*a*′) bond to 1.377 Å, which, as in SP(VII) where the length of this bond is 1.372(3) Å, suggests that the conjugation of the π-UEP of the O(1′) atom with the π-system of the naphthalene ring is weakened. With this type of structure of the spiro centre of SP(XIII), the C(22′)–O(1) bond will be more polar and the π-UEP of the O(1′) atom will be more active, so that in the spiro centre the n[O(1′)]–σ*[C(22′)–O(1)] interactions, which lead to an elongation of the C(22′)–O(1) bond, will predominate. In this case the C(22′)–O(1′) bond proves to be only slightly longer than the normal value of 1.41–1.43 Å.[15–17]

The C(22′)–O(1) bond is elongated in SP(XIII) less than in the correspondig indoline spiropyrans SP(I)–SP(IV) and its length matches the length of the C_{spiro}–O bond [1.452(2) Å] in SP(V), in which the activity of the UEP of the N(1′) atom is less than in SP(I)–SP(IV). These results suggest that the efficiency of the resulting n–σ* interactions in a spiro centre containing two heteroatoms that are both O, despite their different electronic state, is less than in a spiro centre containing O and N atoms. Nevertheless, it opens up the possibility for developing new classes of photochromic SPs containing the same heteroatoms in the spiro centre but in different electronic states. In this case the structure and hence the photochemical properties of such SPs can be regulated by changing the electronic environment of the heteroatoms.

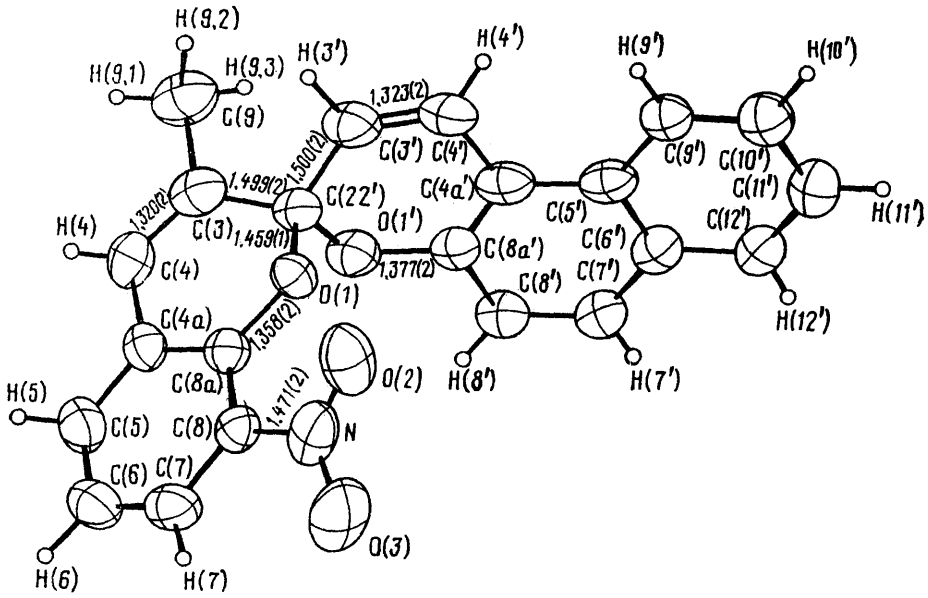
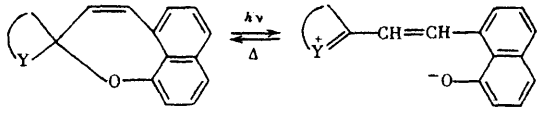


Figure 11. General shape of the "symmetrical" SP(XIII).

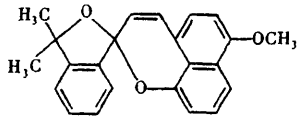
3. Structure of the first example of a spiro-2*H*-naphtho-[1,8-*bc*]oxepin

In accordance with ideas based on quantum-chemical calculations,[68] a long-wavelength band (1500–2000 nm) would be expected to occur in the electronic spectra of zwitterions X.



(Y) (X)

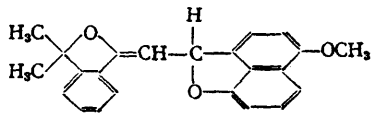
However, for a long time it was not possible to obtain spiropyrans (Y) containing seven-membered rings.[80] In 1986 a spiropyran of this type—SP(XIV)—was obtained for the first time and its structure studied.[81]



SP(XIV)

The general form of SP(XIV) is shown in Fig. 12. The dihedral angle between the O(1)C(22')C(3) and O(2)C(22')C(16) planes is equal to 89.9°. The oxaindan part of the molecule has an envelope configuration with a 25.0° angle of twist from the line of C(22')...C(13). Because of the rigid tetrahedral configuration of the C(22') spiroatom, the seven-membered oxepin ring is severely strained and has a distorted conformation. This type of conformation of the seven-membered ring leads to a change in the relative configuration of the π-UEP of the O(1) atom and the adjacent C(22')–O(2) bond in the spiro centre. While the π-UEP of the O(2) atom is oriented at an angle of 165.0° to the adjacent C(22')–O(1) bond and this proves to be favourable for n^{π}[O(2)]–σ*[C(22')–O(1)] orbital interaction, the π-UEP of the O(1) atom is oriented at an angle of 110.4° to the adjacent C(22')–O(2) bond, which actually suggests that there is no reverse n^{π}[O(1)]–σ*[C(22')–O(2)] interaction. Therefore, in SP(XIV) the efficiency of the interaction between the π-UEP of the O(2) atom and the σ*-orbital of the C(22')–O(1) bond increases, which results in a contraction of the C(22')–O(2) bond to 1.409 Å and an elongation of the C(22)–O(1) bond to 1.455(3) Å.

In the seven-membered ring, with an angle of deviation from the O(1)–C(8*a*) bond of 63.3°, the π-UEP of the O(1) atom is directed inside the heterocycle towards the C(4) atom, although it deviates from the line of O(1)...C(4) by approximately 38°. Taking into account the short interatomic distance of O(1)...C(4) (2.88 Å) and distortion of the C(3)C(4)C(4*a*) bond angle to 130.3°, it may be assumed that there is an attractive secondary interaction between the O(1) atom and C(4) atom destabilising the heterocycle.[79] It would appear that these structural features of SP(XIV) are responsible for its rapid conversion in solution on irradiation with a mercury lamp (313 nm filter) compound (P) rather than compound (Y).[81]



(P)

V. Structure, photo- and thermo-chromic properties of 2-oxaindan spiropyrans with polycondensed chromene residues

1. Structure of 2-oxaindan spiropyrans

It has already been mentioned, that the significant improvement in performance of SPs, and primarily the increase in stability of their

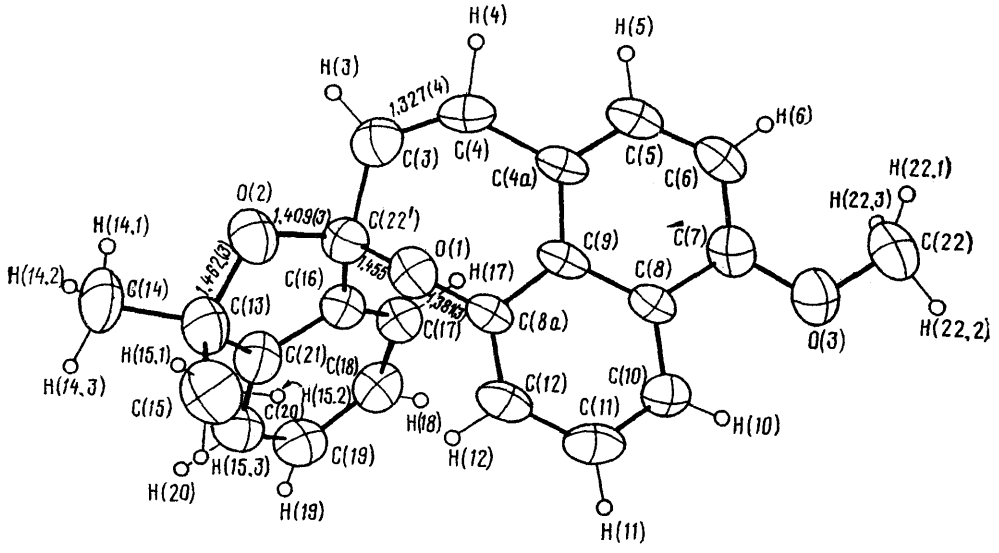
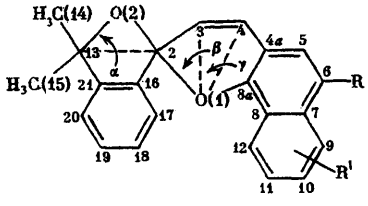


Figure 12. General shape of spiro-2*H*-naphtho[1,8-*bc*]oxepin.

photoinduced forms may be achieved by the introduction of strong electron-acceptor substituents into the benzopyran residue. However, such substituents considerably reduce the photostability of SPs,[63] thus severely limiting in scope the practical application of materials based on them.[83] Hence a study was made of the 2-oxaindan spiropyrans SP(XV)–SP(XVIII), whose photocoloured forms are stabilised through increasing the size of the π-system of the quinoid residue by means of annelation of additional arene rings to the 7,8-bond of the benzopyran part of the molecule.[84]



SP(XV)–(XVIII)

(XV): R = H, R' = H;
(XVI): R = H, R' = 10,11-benzo
(XVII): R = Br, R' = H;
(XVIII): R = NO_2, R' = H.

An X-ray study of SP(XV)–SP(XVIII) showed that these compounds have the same conformation. The naphtho(anthraceno)-pyran and oxaindan parts of the molecule are positioned approximately at right angles to each other. The dihedral angle between the O(1)C(2)C(3) and O(2)C(2)O(16) planes is 93–95°. In all of the SPs studied the pyran and oxaindan residues are nonplanar. The first has a folded conformation with dihedral angles along the lines of O(1)...C(3) and O(1)...C(4) of 21.4 to 28.6° and 10.2 to 13.3° respectively, while the second has the conformation of an envelope with an angle of inflection along the line of C(2)...C(13) equal to 15.5–17.3°. The structure of one of the spiropyrans studied is shown in Fig. 13 and their main structural parameters are given in Table 2.

In the same way as in the previously studied indoline SPs, the C_{spiro}–O(1) bond is elongated in SP(XV)–SP(XVIII). However, while in SP(I)–SP(XI) the lengths of these bonds are in the range 1.460(2)–1.496(4) Å, in SP(XV)–SP(XVIII) these bond lengths are in the range 1.444(1)–1.465(2) Å. At the same time in the unsubstituted SP(XV) this bond [1.444(1) Å] is the least elongated in comparison with the lengths of normal C–O bonds (1.41–1.43 Å) in six-membered heterocycles. Annelation of an additional benzene ring to SP(XVI) has virtually no effect on the length of the C(22')–O(1) bond [1.447(1) Å]. The introduction of electron-acceptor substituents into the 6-position of the naphthopyran residue—Br in SP(XVII) and particularly the NO_2 group in SP(XVIII)—results in this bond being extended to 1.455(3) Å and 1.465(2) Å respectively (Table 2). In the oxaindan residue of SP(XV)–SP(XVIII) the C(22')–O(2) bond was shortened to 1.417(1)–1.407(3) Å compared to the normal length of a C–O bond in five-membered heterocycles (1.426 Å).[85] As the C(22')–O(1) bond increases in length, the C(22')–O(2) bond has a tendency to contract, whereas the O(2)–C(13) bond in these SPs remains elongated (see Table 2).

In the spiro centre of SP(XV)–SP(XVIII) there are two heteroatoms which are both oxygen. In those systems in which two oxygen atoms are bound to an anomeric carbon atom, the efficiency of the $n-\sigma^*$ interaction will primarily depend on the geometric configuration of the UEP of the oxygen atoms and the electronic state of these atoms.

The compounds studied [SP(XV)–SP(XVIII)] have the same conformation with similar values of angles τ and Δ (see Table 2). However, the electronic states of the O(1) and O(2) atoms in them differ substantially. The O(1) atom is bound to the aromatic π-system of the naphthalene or anthracene residues, the bond lengths of O(1)–C(8*a*) [1.354(2)–1.377(1) Å] are similar to the lengths of the corresponding bonds in α-naphthol (1.37 Å)[86] and suggest that there is significant conjugation of the UEP of the O(1) atom with the neighbouring π-system. This conjugation will increase the polarity of the C(22')–O(1) bond relative to the polarity of the C(22')–O(2)

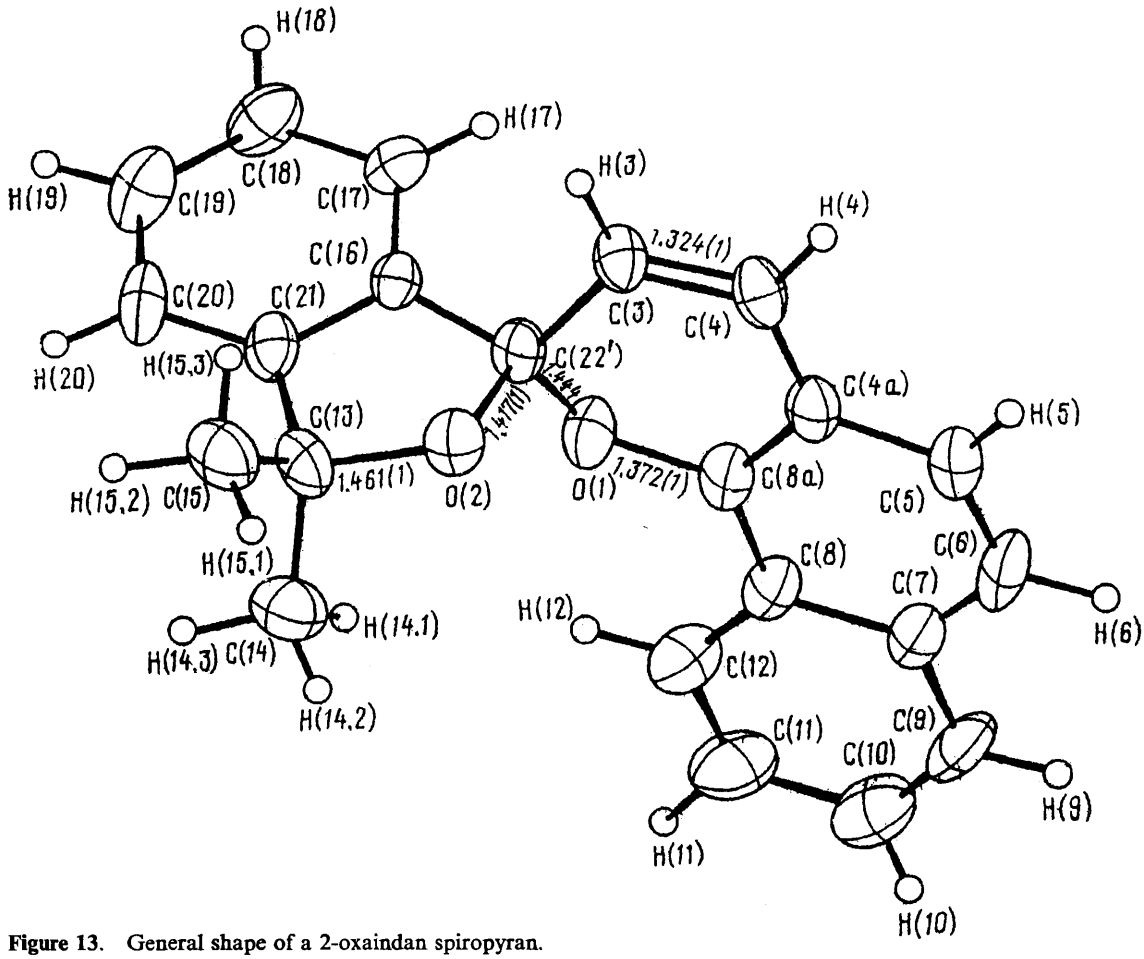
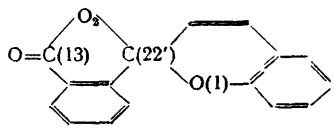


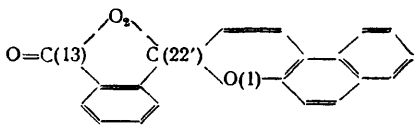
Figure 13. General shape of a 2-oxaindan spiropyran.

bond and decrease the activity of the UEP of the O(1) atom compared to the activity of the UEP of the O(2) atom. Therefore in these spiropyrans the $n[O(2)]-\sigma^*[C(22')-O(1)]$ interactions should be stronger than the $n[O(1)-\sigma^*[C(22')-O(2)]$ interactions and may be responsible for the elongation of the C(22')–O(1) bonds and contraction of the C(22')–O(2) bonds found in these SPs. In the same way as in SP(XIII), these interactions are weaker in SP(XV)–SP(XVIII) than in SP(I)–SP(XI), which contain different heteroatoms (O and N) in the spiro centre, and the lesser elongation of the $C_{spiro}-O(1)$ bond in SP(XV)–SP(XVIII) is related to this.

In SP(XIX) and SP(XX), which were studied previously,[87,88]



СП (XIX)

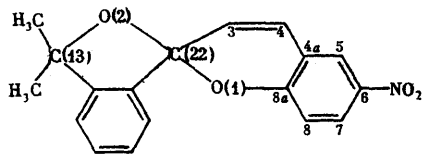


SP(XX)

the π-UEP of the O(2) atom are conjugated with the π-bond of the neighbouring carbonyl group, as is indicated by the length of the O(2)–C(13) bond (1.35–1.37 Å), therefore the $n-\sigma^*$ interactions of the O(1) and O(2) atoms in these molecules are small and the lengths of the C(22')–O(1) bonds (1.42 and 1.399 Å) are of normal magnitude.

Introduction of the electron-acceptor substituents Br and NO_2 into the 6-position of the naphthalene residue gives rise to an elongation of the C(22')–O(1) bond, which increases as the electron-acceptor properties of the substituents increase [1.455(3) Å in SP(XVII) and 1.465(2) Å in SP(XVIII)]. At the same time there is a contraction of the O(1)–C(8*a*) bond to 1.366(3) Å in SP(XVII) and 1.354(2) Å in SP(XVIII) compared to the length of this bond in SP(XV) and SP(XVI), in which it amounts to 1.372(1) and 1.377(1) Å respectively. This suggests that there is an increase in conjugation of the UEP of the O(1) atom with the π-system of the naphthalene residue on introduction of electron-acceptor substituents, so the elongation of the C(22')–O(1) bond in SP(XVII) and SP(XVIII) is related to the strengthening of the $n[O(2)]-\sigma^*[C(22')-O(1)]$ interaction in these compounds, which also results in a contraction of the C(22')–O(2) bond in SP(XVII) and SP(XVIII) to 1.413(3) and 1.407(3) Å respectively in comparison with the length of this bond in SP(XV) and SP(XVI), where it is equal to 1.417(1) Å.

It is interesting that in the analogous benzopyran SP(XXI)[89]



SP(XXI)

with an NO_2 group at the *para*-position relative to the O(1) atom, the C(22′)–O(1) bond is less elongated (1.452 Å) and the O(1)–C(8*a*) bond (average 1.366 Å) is less contracted than in SP(XVIII). These results suggest that the electron-acceptor effect of the NO_2 group on the O atom is more marked in a naphthalene residue than in a benzene residue.

In order to confirm the electronic rather than steric nature of the elongation of the C(22′)–O(1) and O(2)–C(13) bonds and contraction of the C(22′)–O(2) bond, conformational calculations on a model SP were carried out.[84] After minimisation of the energy of strain in the molecule the length of the C(22′)–O(1) bond in it proved to be of normal magnitude (1.422 Å) while the lengths of the C(22′)–O(2) (1.434 Å) and O(2)–C(13) (1.439 Å) bonds were the same and close to normal values.

2. Thermal valence isomerisation of SPs

Spiropyrans SP(XV)–SP(XVIII) have distinct thermochromic properties in solutions of polar and nonpolar solvents. From the values calculated from dynamic NMR data for the free energy of activation of thermally induced valence isomerisation of SP(XV)–SP(XVIII)[84] and certain other SPs that were studied[90] and comparing them with the lengths of the C_{spiro}–O(1) bonds in these compounds the following conclusions could be drawn:

1) a variation in structure of the heterene and pyran residues of the SP molecule has no substantial effect on the free energy of activation of the SP;

2) there is no correlation between the C_{spiro}–O(1) bond length in SP(XV)–SP(XVIII) and the free energy of activation.

The lack of this correlation, which was also predicted from quantum-chemical calculations,[91] evidently arises because the C_{spiro}–O(1) bond length in the ground transition state (the region of thermochromic cleavage), as was demonstrated by Simkin et al.,[46] is almost constant (~1.95 Å) and differs considerably from the length of this bond in the initial state. Therefore the small changes in length of this bond which occur as a result of structural factors do not have any substantial effect on the energy of activation for cleavage of this bond.

3. Photochromism of 2-oxaindan spiropyrans

The photochromic properties of SP(XV)–SP(XVIII) in liquid and solid solutions are exhibited over a wide temperature range (from 77 to 273 K). By using the technique of flash photolysis it is possible to observe reversible photocoloration even at 20 °C. In order to determine the relative photochemical activity of SP(XV)–SP(XVIII), Aldoshin et al.[84] studied the ease of photocoloration ("colorability") of these compounds. The results of a study of the "colorability" of SP(XV)–SP(XVIII) compared to the C_{spiro}–O(1) bond length are given in Table 3. It is clear from Table 3 that these values vary in a similar manner, the highest photochemical activity being exhibited by SP(XVIII) with the most elongated bond. This apparently occurs because the C_{spiro}–O(1) bond length in the excited transition state is much shorter than that in the ground transition state. Consequently, the reaction barriers of SPs in the excited states are markedly reduced. Therefore the photochemical activity for coloration of an SP proves to be sensitive to even small changes in the C_{spiro}–O(1) bond length in the ground state, which result from the influence of different structural factors in SP molecules.

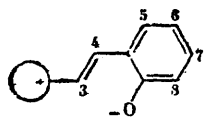
Unfortunately, it was not possible to carry out an X-ray diffraction study of the resulting open coloured form of 2-oxaindan SPs, and the structure of the coloured products can only be assessed

Table 2. Main structural parameters of 2-oxaindan spiropyrans studied.

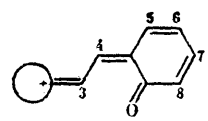
SP	Substituents		Bond lengths*1, Å				Angles, deg				
	R	R′	C(22′)–O(1)	C(22′)–O(2)	O(1)–C(8*a*)	O(2)–C(13)	α	β	γ	τ*2	Δ*3
(XV)	H	—	1.444	1.417	1.372	1.461	17.3	21.4	10.2	159.6	159.8
(XVI)	H	10,11-benzo	1.447	1.417	1.377	1.461	16.3	22.2	10.3	158.4	159.8
(XVII)	Br	—	1.455	1.413	1.366	1.457	16.1	26.8	13.3	158.9	155.7
(XVIII)	NO_2	—	1.465	1.407	1.354	1.458	15.5	28.6	11.4	160.1	155.5

*1 Errors in determining the bond lengths constitute 0.001–0.003 Å.
*2 Angle between the π-UEP of the O(2) atom and the C(2)–O(1) bond.
*3 Angle between the π-UEP of the O(1) atom and the C(2)–O(2) bond.

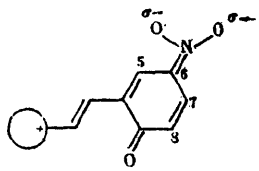
from indirect evidence. The X-ray diffraction study of the open forms of indoline SPs showed that they have the zwitterion structure (A) with an appreciable contribution from the canonical structure (C).



(A)



(B)



(C)

However, in contrast to indoline SPs, SP(XV)–SP(XVIII) and SP(XXII) reveal bathochromic shifts of the photoinduced absorption bands on increasing the polarity of the medium, regardless of the nature of the substituents.[92] These findings suggest that the quinoid structure makes a decisive contribution to the structure of the coloured form. It was suggested above (see Section III) that annelation of additional benzene rings to the phenolate residue at the 5,6- and 7,8-positions should stabilise the quinoid structure (C) while annelation at the 6,7-position would destabilise this structure. The increase in the lifetime of SPs on going from SP(XV) to SP(XVI) supports this view and is an indication of the important role of this method for stabilising an open SP form.

Table 3. "Colorability" of spiropyrans SP(XV)–SP(XVIII) and the C_{spiro}–O(1) bond length.

SP	"Colorability"*	C_{spiro}–O(1) bond length, Å
(XV)	0.22	1.444 (1)
(XVI)	0.32	1.447 (1)
(XVII)	0.36	1.455 (3)
(XVIII)	0.46	1.465 (2)

*The colorability is determined from the initial absorption A_0 of solutions of photochromic SPs under exactly the same irradiation conditions (temperature, SP concentration, length and volume of cell, irradiation intensity). Indoline SP(IV) is most frequently used as the reference compound, for which $A_0 = 1$.

The introduction of electron-acceptor substituents into the naphthopyran residue of these SPs also increases the lifetime of the open forms. The nitro group with its strong electron-acceptor properties has the greatest stabilising effect. As in indoline SPs, the stabilisation of the coloured products of SP(XVIII) with electron-acceptor substituents appears to be related to the increased contribution of the resonance form (C) to their structure.

An additional factor for stabilisation of the coloured forms of these SPs may also be the formation of different intermolecular associates, as takes place for the open merocyanine forms of indoline SPs. At the same time, the more extended the conjugated π-system of the SP, the more stable (through π–π interaction) may be the associates.

VI. Conclusion

Thus, as a result of analysing the structure of different classes of spiropyrans, the structural factors which affect their photochemical properties have been established.

It has been shown that the photochemical properties of spiropyrans in many respects is due to the fact that even in the ground state the C_{spiro}–O bond, which undergoes cleavage on photoexcitation, is weakened and elongated through specific $n-\sigma^*$ orbital interactions, which on going to excited photochemically active states are even further strengthened, thus assisting the cleavage of this bond. It has been established that the photochemical activity of spiropyrans depends on the length of the C_{spiro}–O bond in the ground state and the nature of the change in length of this bond in the excited state. At the same time the photochemical activity of spiropyrans proves to be more sensitive to the length of the C_{spiro}–O bond being cleaved than does the thermochromic activity.

A study has been made of the effect of different substituents in the benzopyran and indoline residues, the nature, electronic state, and relative orientation of the heteroatoms in the spiro centre, and the size of the heterocycles on the efficiency of $n-\sigma^*$ interactions in spiropyran molecules and on the length of the C_{spiro}–O bond in the ground state.

The structure of the photoconversion products of spiropyrans and the stereochemical factors responsible for stabilising it have been examined. For the coloured photoforms of spiropyrans in the crystalline state the formation of different strong intermolecular associates and solvates has been detected, which to a considerable degree govern the stabilisation of the complex resonance structure of spiropyrans not only in the crystalline state but also in solution, which is a more probable cause of the complex absorption spectrum of these compounds than the proposed existence of various isomers.

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The structure of novel conductive dithiolate complexes

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ABSTRACT. The characteristics of the molecular and crystalline structure of novel transition metal dithiolate complexes are examined and the correlation between structure and electrical conductivity of these compounds is discussed. The material reviewed is of interest both for the crystal chemistry and physical chemistry of the respective class of molecular conductors and for the structural chemistry of dithiolates.

The bibliography includes 94 references.

Contents

I. Introduction 686
II. Structure of salts of 4,5-dimercapto-2-thione-1,3-dithiolates with "closed" cations 687
III. Structure of salts of 4,5-dimercapto-2-thione-1,3-dithiolates with "open" cations 695
IV. Crystalline structures of 5,6-dihydro-1,4-dithiin-2,3-dithiolate complexes and their salts 700
V. Conclusion 704

I. Introduction

Solid-state reactions are of increasing interest to research workers. This is because the limited mobility of reacting molecules in a crystal makes it possible to carry out a successive structural study of a whole chain of molecular reactions and to obtain polymers of a regular structure, large, defect-free monocrystals, etc. This is all due to the origination and development of a new branch of science—crystal engineering—which is aimed at studying the principles and laws governing the formation of those types of packing of potentially reactive molecules and crystals in which favourable conditions are created for the molecules to participate in given reactions and rearrangements.[1–21]

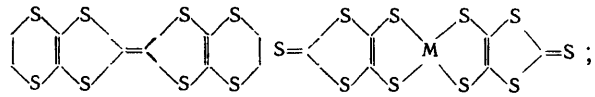
At the present time the concepts of crystal engineering have been developed further in studies on crystalline low-dimensional semiconductors, metals, and superconductors. Special emphasis has been given to research on the properties of this promising class of organic materials (the design of molecular "corridors" of the primary movement of electrons, the use of heteroatoms for achieving overlap of orbitals of neighbouring molecules, the elimination of spatial modulation of charge density by changing the intermolecular distances, etc.).

The structure and packing of donor and acceptor molecules in crystals of organic conductors have a number of specific features. Donor molecules should be planar and include π-residues and heteroatoms (nitrogen, oxygen, or chalcogen atoms). For acceptor molecules the shape, size, and charge are important. In the crystal the donor and acceptor molecules should be located so as to achieve the necessary electronic interaction for delocalisation of electrons and high electrical conductivity. In other words, the molecular building blocks of an organic conductor should be well suited to achieve overlap between the π-electron systems of neighbouring molecules. By changing the structure of donor and acceptor molecules and also the conditions for obtaining the organic conductor that affect its composition (the ratio of donor to acceptor), it is possible to vary the crystalline structure, and this in turn leads to a change in the degree of charge transfer and electrical conductivity of the crystal under these conditions. As examples of the "active" modification of the properties of an organic metal (or superconductor) through alteration of the molecular structure of its components, mention can be made, for example, of the change from salts of the type TTF–TCNQ to the salts $(TMTSF)_2X$ (for notation see Table 1), the structure of which exhibits more pronounced two-dimensional characteristics as a result of introducing Me groups and Se atoms into the donor molecule and replacing acceptors of the type TCNQ by monovalent anions of the type X = PF_6;[22–24] the change from salts of the type $(TMTSF)_2X$ to salts of the type $(BEDT–TTF)_2Y_3$, which have a stronger interstack interaction and a higher value of the transition temperature to a superconductive state (T_c) as a result of replacement of the donors TMTSF by BEDT–TTF;[25–27] and the further increase in T_c in $(BEDT–TTF)_2Y_3$ salts by altering the Y_3 anions ("chemical compression" effect).[28–31]

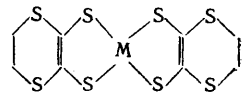
At the present time organic metals and superconductors in which BEDT–TTF acts as the donor have been studied the most actively. In contrast to conductive radical cation salts with packing in stacks (perylenium salts, for example),[32] in crystals of BEDT–TTF salts the central π-electron system of the molecule† is not involved in intermolecular interaction. On the other hand, in conductive crystals, the so-called one-dimensional transition metal complexes with organic ligands, the conductive corridors are in fact produced from the electrons of the "central" metal ions interacting with their neighbours in the stack situated above and below the central ion. The organic ligands do not participate in intermolecular electron transfer.[33] It was natural that the idea of synthesising compounds that would simultaneously combine the properties of salts of the type BEDT–TTF and those of one-dimensional metal complexes should develop (see, for example, the study of Keller et al.),[34] and this was carried out at approximately the same time by different groups of research workers. They synthesised transition metal complexes with novel sulphur-containing ligands such as $[M(dmit)_2]^n$ and

†In this and other cases (which will subsequently not be mentioned separately) we are, of course, dealing with a radical ion (in this case the radical cation $BEDT–TTF^{+\cdot}$) that is called a "molecule" in order to simplify the discussion of the crystalline structure in terms of the crystal chemistry of molecular crystals.

$[M(DDDT)_2]^n$. Their salts have a close structural similarity to salts of BEDT–TTF.



BEDT—TTF $[M(dmit)_2]^n$



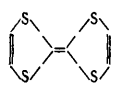
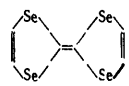
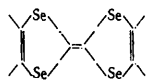
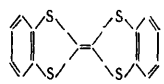
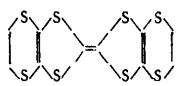
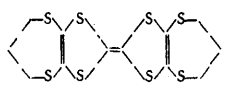
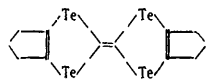
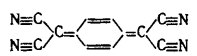
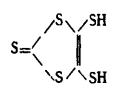
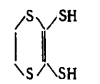
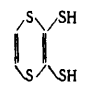
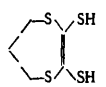
$[M(DDDT)_2]^n$

The complexes $[M(dmit)_2]^n$ and $[M(DDDT)_2]^n$ belong to a well-known class of dithiolate complexes. The structure of simpler dithiolate complexes has been discussed several times (see, for example, two studies[35,36]). Thus, their molecules or ions were observed to have an overall planar structure regardless of the nature of metal or its degree of oxidation, a capacity for reversible electron transfer reactions with the formation of stable products, considerable delocalisation of the π-type HOMO, and a high electron-acceptor capacity relative to organic donors.

Dithiolate complexes have considerable structural flexibility (geometric and electronic) with regard to replacement of the central metal atom and the substituents in the ligands and counterions.

In this review the literature data and the present authors' own results in studies on the structure of novel sulphur-containing dithiolate complexes of the type $[M(dmit)_2]^n$ and $[M(DDDT)_2]^n$ and on the search for correlations between structure and electrical conductivity are examined.

Table 1. Notation used in this review.

Name	Structural formula	Notation
Tetrathiafulvalene		TTF
Tetraselenafulvalene		TSF
Tetramethyltetraselenafulvalene		TMTSF
Dibenzotetrathiafulvalene		DBTTF
Bis(ethylenedithio)tetrathiafulvalene		BEDT—TTF
Bis(propylenedithio)tetrathiafulvalene		BPDT—TTF
Bis(trimethylene)tetratellurafulvalene		HMTTeF
Tetracyanoquinodimethane		TCNQ
4,5-Dimercapto-1,3-dithiole-2-thione		H_2dmit
5,6-Dihydro-1,4-dithiin-2,3-dithiol		H_2DDDT
1,4-Dithiin-2,3-dithiol		H_2DDT
5,6-Dihydro-1,4-dithiepin-2,3-dithiol		H_2DDTDT

II. Structure of salts of 4,5-dimercapto-2-thione-1,3-dithiolates with "closed" cations

Table 2 lists the main data on the structures and conductivity of $Cat_x[M(dmit)_2]^{x-}$ salts, formed with "closed" cations. These are cations of the type Me_4N^+, Et_4N^+, Me_3S^+, Ph_4As^+, etc., which, in contrast to cations (donors) of the type TTF, TMTSF, and BEDT–TTF, are incapable of intermolecular electron transfer. Since in all cases Cat is a single-charged cation, the value of x is equal to the formal average negative charge of the complex anion $[M(dmit)_2]^{x-}$. In the crystal of the neutral complex $Ni(dmit)_2$ (I)[37] the molecules are arranged in a displaced manner in stacks, the normal to the plane of the complex forms an angle of 48.0° with the [010] direction. There is one shortened intermolecular S...S contact (3.577 Å) within a stack and three contacts between stacks (3.580, 3.580 and 3.575 Å). In the opinion of Valade et al.,[37] the interstack contacts have a short length because they are formed by the thione S atoms and the corresponding S...S vectors are aligned at considerable angles to the plane of complex (I) (far from parallel to this plane).‡ In other words, because of the anisotropy in the relative orientation of the π-atomic orbitals of the atoms in different molecules, even close contacts can lead to small values of the electron hopping parameter.

It has been observed by Valade et al.[37] that the crystal of (I) meets the structural requirements needed for highly conductive systems (the occurrence of regular stacks and reduced intermolecular distances) but it does not satisfy the main electronic criterion—the occurrence of a fractional charge, which accounts for the low conductivity of (I) ($\sigma \sim 3.5 \times 10^{-3}$ Ω^{-1} cm^{-1}).§ Localisation of a

‡In an analysis of the crystalline structure of organic conductors, the interaction (orbital overlap) between neighbouring molecules is determined by comparing the intermolecular distances with the sum of the van der Waals radii of the atoms (see, for example, Pauling[51]). In molecular crystals at room temperature the orbital overlap is small if the intermolecular distances are greater than the sum of the van der Waals radii. At distances smaller than the sum of the van der Waals radii, the contribution of orbital overlap increases exponentially.[52] In addition to the absolute values of the intermolecular distances it is also necessary to take into account the relative orientation of the orbitals of the molecules in contact (see, for example, the study of Mori et al.[53]) in a determination of orbital overlap.

§The specific conductivity σ of insulators varies over the range $10^{-22}-10^{-15}$ Ω^{-1} cm^{-1}, for semiconductors it varies over the range $10^{-8}-10^{-2}$ Ω^{-1} cm^{-1} (increases as the temperature is increased), and for metals the variation is $10-10^4$ Ω^{-1} cm^{-1} (increases as the temperature is lowered).

Table 2. The main data on $Cat_x[M(dmit)_2]^{x-}$ compounds.

Compound	Chemical formula	Structural motif	d, Å*	M–S distances, Å	Conductivity σ_{293}, Ω^{-1} cm^{-1}	Refs.
(I)	$Ni(dmit)_2$	Stacks	3.56	2.147(2)	$3.5\cdot10^{-3}$	[37]
(II)	$(Me_4N)_{0.5}[Ni(dmit)_2]$	" Layers	3.53; 3.58	2.158	50	[38, 39]
(III)	α-$\{(Me_2Et_2N)_{0.5}[Ni(dmit)_2]\}$	Stacks Layers	3.52	see**	20–100	[40]
(IV)	$(Et_4N)_{0.5}[Ni(dmit)_2]$	Stacks Layers	3.44; 3.76	2.146–2.154(3)	$4.5\cdot10^{-2}$	[41]
(V)	$(Bu_4N)_{0.29}[Ni(dmit)_2]\cdot MeCN$	Stacks Layers	3.51–3.57	2.153(4)	1–10	[37, 42]
(VI)	$(Bu_4N)_2[Ni(dmit)_2]$	Not formed	—	2.211; 2.221(6)	see**	[43]
(VII)	$(Bu_3S)[Ni(dmit)_2]$	Dimers	3.63	2.161–2.174(2)	10^{-6}	[44]
(VIII)	$(Ph_4As)_{0.25}[Ni(dmit)_2]$	Stacks Layers	3.50–3.61	2.152–2.171(6)	10–15	[45]
(IX)	$(Bu_4N)[Pt(dmit)_2]$	Chains	—	see**	$<10^{-8}$	[46]
(X)	α-$\{(Et_4N)_{0.5}[Au(dmit)_2]\}$ [isostructural to (IV)]	Stacks Layers	3.79; 3.49	2.314–2.321(1)]	0.2	[47]
(XI)	$(Et_4N)[Au(dmit)_2]$	Stacks	3.64; 3.57	2.311–2.320(2)	10^{-5}	[48]
(XII)	$(Bu_4N)[Au(dmit)_2]$	Chains	—	2.316–2.327(4)	see**	[49]
(XIII)	$(Me_3S)[Au(dmit)_2]$	Thin layers	3.59	2.307–2.323(3)	10^{-6}	[50]
(XIV)	$(Bu_3S)[Au(dmit)_2]$ [isostructural to (VII)]	Dimers	3.67	2.304–2.319(2)	10^{-6}	[44]

*Interplanar distance (between planes of neighbouring anions in a stack or between planes of layers) is given.
**These figures were not given in the original study.
***Insulator.

fractional charge on donor and acceptor molecules in the crystal of an organic metal assists the formation of vacancies on to which electrons can hop at sufficiently high values of the resonance parameters.

In the crystal of $(Me_4N)_{0.5}[Ni(dmit)_2]$ (II) the almost planar $[Ni(dmit)_2]^{1/2-}$ complexes are stacked along the [110] direction. The distances between the planes of the complexes in the stacks alternate between 3.53 and 3.58 Å (Fig. 1). The reduced intermolecular S...S contacts combine the stacks of anions into layers parallel to the (001) plane and alternating along the [001] direction) with layers of Me_4N^+ cations.

The electrical conductivity of the crystal of (II) in a plane parallel to the planes of the layers [parallel to the (001) plane of the crystal] is $\sim 50\ \Omega^{-1}$ cm^{-1} at room temperature, while in a plane perpendicular to the (001) plane it is $\sim 10^{-2}\ \Omega^{-1}$ cm^{-1}. At 100 K the crystal of (II) undergoes a metal–semimetal transition (concentration of conducting electrons decreases to $10^{-3}-10^{-5}$ electrons per atom) and the electrical conductivity along the planes of the layers falls to $1.4\times10^{-2}\ \Omega^{-1}$ cm^{-1}, with the resistance in the plane perpendicular to the layers remaining approximately 10^3 times higher in value.

The stacks of anions directed along [110] and [1$\bar{1}$0] alternate in the [001] direction. Significant is the absence of satellite reflections on the X-ray photographs of samples of (II) when they are cooled below 100 K, where the crystal of (II) undergoes a metal–semimetal transition. X-Ray diffraction analysis of a sample of (II) carried out at temperatures above (293 K) and below (92 K) the transition temperature did not reveal any structural differences in the crystal on changing the temperature.

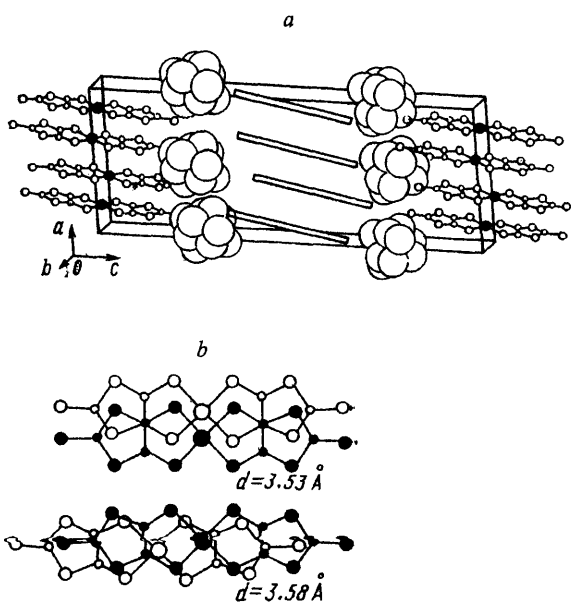


Figure 1. The structure of crystals of $(Me_4N)_{0.5}[Ni(dmit)_2]$ (II) at 95 K (*a*) and the two ways in which the $[Ni(dmit)_2]^{1/2-}$ anions are superimposed in stacks along the [110] direction[38,39] (*b*). The van der Waals spheres of the H atoms in the disordered Me_4N^+ cations are depicted as large circles. The anions perpendicular to the plane of Fig. 1 are shown as rods.

The dependence of the resistance of the crystal of (II) on pressure was studied up to a pressure of 7 kbar. On increasing the pressure the metal–semimetal transition is suppressed and above 3 kbar phenomena characteristic of a superconductive transition occur. At 7 kbar the transition temperature (T_c) was 5 K and the value of dT_c/dP for complex (II) was greater than zero. A positive value of dT_c/dP also occurs for $(TTF)_{0.5}[Ni(dmit)_2]$,[38,39] while for the salts $(TMTSF)_2X$ (X = ClO_4, PF_6, and others)[54] and β-(BEDT–TTF)$_2$X (X = I_3, IBr_2)[55] this value is less than zero.

The hysteresis from continuous heating and cooling a crystal of (II) over the range from about 90 to 300 K is attributed by Kobayashi et al.[39] to the rotational randomisation of the Me groups at room temperature, frozen out on cooling the samples to 95 K.

Compound (II) is the first molecular superconductor to consist of π-acceptor molecules and cations of a closed type.[39] Molecular superconductors consisting of π-donor molecules and closed anions [for example, Bechgaard salts $(TMTSF)_2X$] have previously been reported.[22–24]

In the crystal of α-{$(Me_2Et_2N)_{0.5}[Ni(dmit)_2]$} (III), obtained by electrochemical oxidation of the salt $(Me_2Et_2N)[Ni(dmit)_2]$, the planar $Ni(dmit)_2$ anions are arranged along the *b* axis in stacks in which two types of orbital overlap occur (Fig. 2) through intermolecular S...S contacts (3.424–3.605 Å). Overlap of type (A) occurs between a reference $Ni(dmit)_2$ molecule and two molecules that are not completely parallel to it (dihedral angle 171°), located above the reference one on the *b* axis (lapped overlap). Overlap of type (A) leads to the stacks being combined into layers. Overlap of type (B) takes place between a reference molecule and a molecule parallel to it which is located below on the *b* axis (interplanar distance *d* = 3.52 Å). In a crystal of (III) there are also very short intermolecular S...S distances (3.352 Å) between the thione S atoms of molecules in different layers along the *a* axis.

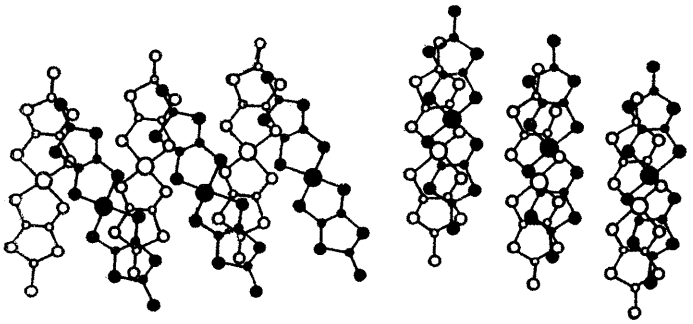


Figure 2. The two ways (*A* and *B*) in which the $[Ni(dmit)_2]^{1/2-}$ anions are superimposed in the crystal of (III).[40]

The electrical conductivity of crystals of (III) in the *bc* plane is isotropic, where σ_{293} = 20–100 Ω^{-1} cm^{-1}; this type of electrical conductivity (typical for metals) is retained down to 1.5 K and a metal–insulator transition does not occur. The electrical conductivity of crystals of (III) along the *a* axis is also quite high: σ_{293} = 1 Ω^{-1} cm^{-1}. At 1.5 K a superconductive transition occurs. Calculation of the overlap integrals of the LUMOs forming the conductivity zone using the extended Hückel (EH) method confirmed the essentially two-dimensional nature of the zone structure in crystals of (III). However, crystals of (III) differ from other $Cat_x[M(dmit)_2]^x$ salts in that for the first time a clear but small interaction was also observed in them in a "third" direction (along the *a* axis).

According to calculations[56] of the intermolecular overlap integrals of the LUMOs in crystals of a number of salts of $M(dmit)_2$ complexes it was found that the b_{2g} symmetry characteristic of these orbitals is not conducive for their overlap in the direction of the short axes of the planar molecules, which is not consistent with the formation of two-dimensional conductive motifs. However, the "lapped" overlap occurring in the crystal of (III) may be regarded as one of the ways of forming two-dimensional motifs.

In the crystal of (IV), which contains the larger Et_4N^+ cations, the $[Ni(dmit)_2]^{1/2-}$ anions are stacked along the [010] direction (Fig. 3).[41] In the stacks there are shortened intermolecular distances between molecules A and B′ but not between molecules A and B. The corresponding interplanar distances are equal to 3.437 Å (between A and B′) and 3.759 Å (between A and B), namely, the anion stacks consist of weakly bound dimers. There are a large number of shortened intermolecular S...S distances between the stacks of anions, as a result of which layers of interacting anions are formed parallel to the (100) plane in the crystal of (IV).

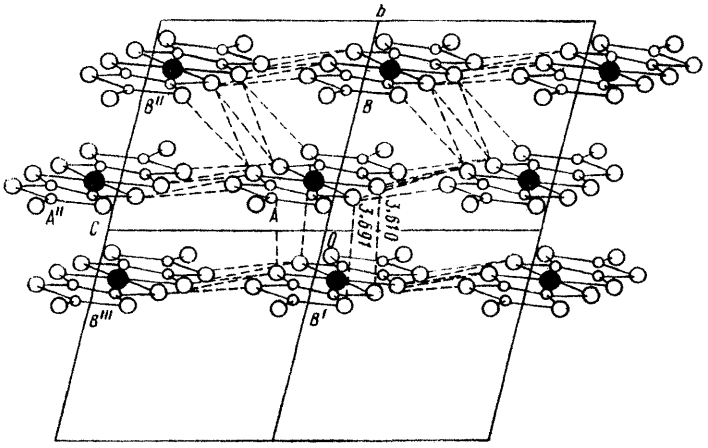


Figure 3. Projection of the crystalline structure of $(Et_4N)_{0.5}[Ni(dmit)_2]$ (IV) on to the *bc* plane (the Et_4N^+ cations are not shown).[41] Here and subsequently shortened intermolecular S...S contacts are indicated by broken lines.

It should be noted that the shortest S...S contacts occur between the "inner" S atoms of the $[Ni(dmit)_2]^{1/2-}$ complexes (3.499 Å), whereas the distances between the "outer" S atoms are more than twice the van der Waals radius of the S atom. Thus, the inner S atoms of the $[Ni(dmit)_2]^{1/2-}$ complexes play a more important role in interstack contacts.

The $[M(dmit)_2]^{x-}$ anions (*x* = 0, ... 1) in crystals of (I)–(VIII) are virtually planar. The bond lengths in the chelate centres of dithiolene complexes of transition metals vary according to their degree of oxidation.[41] The Ni–S distance [2.147(2) Å] in (I) is at the lower limit of the range of Ni–S distances in complexes (I)–(VIII). When the negative charge of the $[Ni(dmit)_2]^{x-}$ complex

is increased, in general there is a tendency for the Ni–S distances to increase (see Table 2). In both the neutral complex (I) and the negatively charged complex (IV) (x = ½), delocalisation of electron density through the chelate residues of the type (Ni)S⋯C⋯C⋯S(Ni) is substantial; the C=C bond lengths are increased to 1.391(9) Å in a crystal of (I) and to 1.39(1) and 1.40(1) Å in (IV), and the (Ni)S–C bond is shortened to 1.699(7) Å in (I) and to 1.682–1.701(7) Å in (IV) compared to the (S=C)S–C bonds in (I) [1.731(7) Å] and in (IV) [1.725–1.732(7) Å]. In the different salts of the anionic $[M(dmit)_2]^{x-}$ complexes the degree of delocalisation through the chelate residues of dithiolene complexes is apparent to a different extent (see below).

The crystal of (IV) is a semiconductor with a low anisotropy of conductivity. The maximum value of electrical conductivity occurs in the plane of the *ac* layer along the stacks ($\sigma_b = 4.5 \times 10^{-2}$ Ω^{-1} cm^{-1}), the energy of activation of electrical conductivity along the *a*, *b*, and *c* axes is 0.15, 0.16, and 0.16 eV respectively. At 300 K $\sigma_a : \sigma_b : \sigma_c = 1 : 50 : 8$.

The intermolecular overlap integrals (S) of the LUMOs of neutral $Ni(dmit)_2$ molecules placed in the positions occupied by the corresponding anions in the crystal of (IV) have been calculated using the extended Hückel method. The values of S for the molecules within the stacks [S(A–B′) = 9.06×10^{-3}, S(A–B) = -2.06×10^{-3}] are higher than those between stacks [S(A–A″) = 1.17×10^{-3}, S(A–B″) = 0.89×10^{-3}, S(A–B‴) = 0.27×10^{-3}], which is consistent with the direction of maximum electrical conductivity.

The crystal of $(Bu_4N)_{0.29}[Ni(dmit)_2]$.MeCN (V) contains eight crystallographically independent $[Ni(dmit)_2]^{0.29-}$ anions (j = 1–8), two of which (j = 1 and 5) are located at centres of symmetry, two crystallographically independent Bu_4N^+ cations, and two MeCN solvate molecules. In all of the (Ni)S⋯C⋯C⋯S(Ni) chelate residues conjugation is clearly apparent—the C=C, (Ni)S–C, and (S=C)S–C distances are (on average) equal to 1.39(2), 1.70(2), and 1.74(2) Å respectively.

The $[Ni(dmit)_2]^{0.29-}$ anions are arranged along the [110] direction into stacks of two types (Fig. 4). In the stacks centrosymmetric triads and tetrads of complexes alternate. The axes of the triads and tetrads are parallel and form angles of ~21° with the plane of the [110] stack. The distances between the mean planes of the complexes in the stacks, which vary from 3.48 to 3.57 Å, are typical for a strong intermolecular π-interaction; for example, in the crystal of (TTF)$[Ni(dmit)_2]_2$ (XV), which has the conductivity of a metal, the interplanar distance in a regular stack is 3.55 Å.[57] According to Soos et al.,[33] an irregular stack structure [both in terms of the interplanar distances (Fig. 4) and the nature of the molecular overlap] is probably responsible for the "nonmetallic" nature of the conductivity in the crystal of (V).

The large number of shortened interstack S...S contacts (34 of the 39 interanion S...S contacts, less than 3.60 Å, relate to contacts between stacks, the shortest of these contacts being 3.442 Å) combine the stacks of $Ni(dmit)_2$ complexes in the crystal of (V) into layers parallel to the (001) plane and separated by layers of Bu_4N^+ cations and MeCN solvate molecules.

Crystals of (V) have a thermally activated (E_a = 0.02–0.1 eV) electrical conductivity σ_{300} = 1–10 Ω^{-1} cm^{-1}. The weak electroconductive anisotropy observed ($\sigma_a/\sigma_b \approx 1$) is consistent with the two-dimensional nature of the structure of (V). The low electrical conductivity in the third direction (along the *c* axis, $\sigma_{300} \approx 10^{-3}$ Ω^{-1} cm^{-1}) is due to the presence of barrier layers of Bu_4N^+ cations and MeCN molecules parallel to the (001) plane.

The Ni–S distances [2.211 and 2.221(6) Å] in the $[Ni(dmit)_2]^{2-}$ anion of the crystal of (VI)[43] are greater than the distances that occur in the $[Ni(dmit)_2]^{x-}$ anions of other complexes (see Table 2) that have a lower negative charge. Information is available[43] on this type of relationship between the Ni–S distances and charges on the anions in simpler dithiolate Ni complexes. The (Ni)S–C distances in the crystal of (VI) [1.74 and 1.76(1) Å] are greater than the

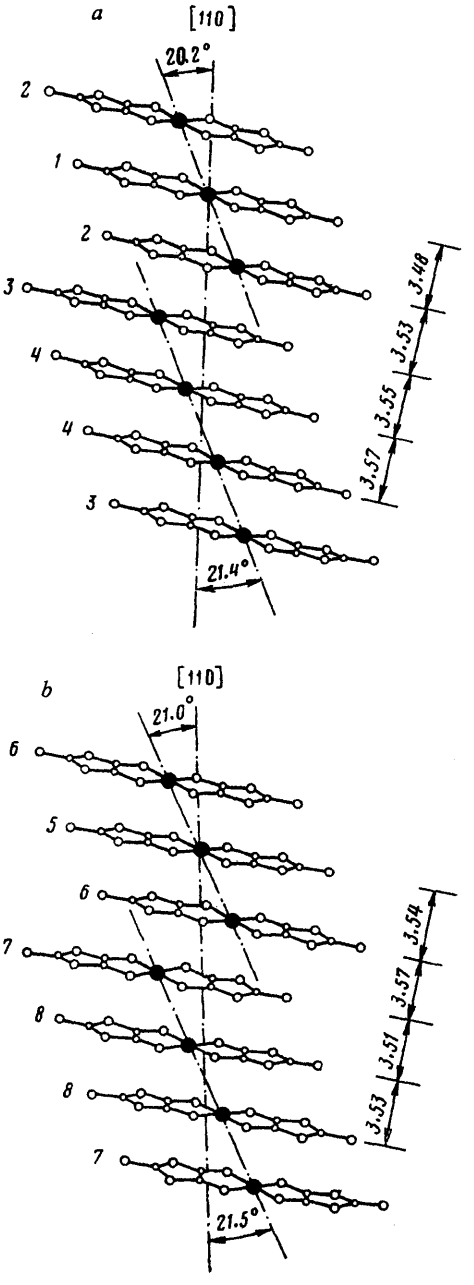


Figure 4. Packing of planar $Ni(dmit)_2$ complexes in the crystal of $(Bu_4N)_{0.29}[Ni(dmit)_2]$.MeCN (V) in stacks of two types (*a* and *b*) along the [110] direction. A projection on to the plane including the [110] vector and the long axis of the complex (the line joining the thione S atoms) is given.[37]

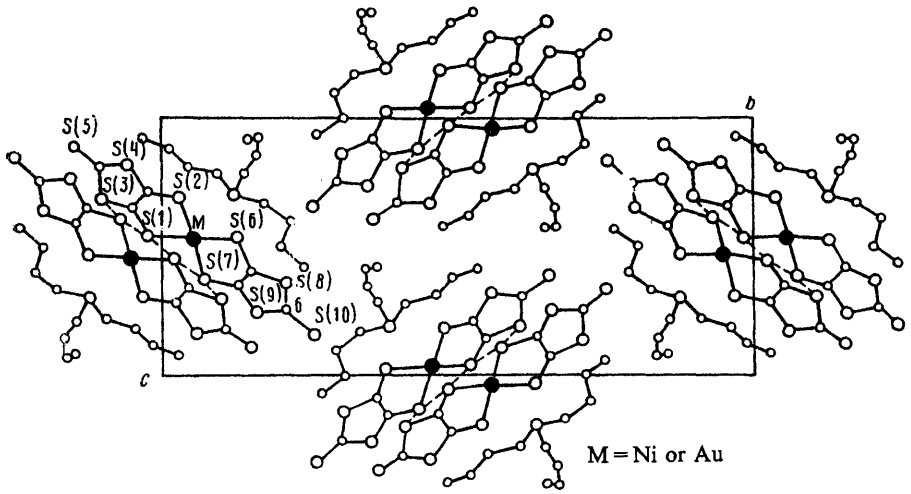


Figure 5. Projection of the isostructural crystals of $(Bu_3S)[Ni(dmit)_2]$ (VII) and $(Bu_3S)[Au(dmit)_2]$ (XIV) on to the *bc* plane.

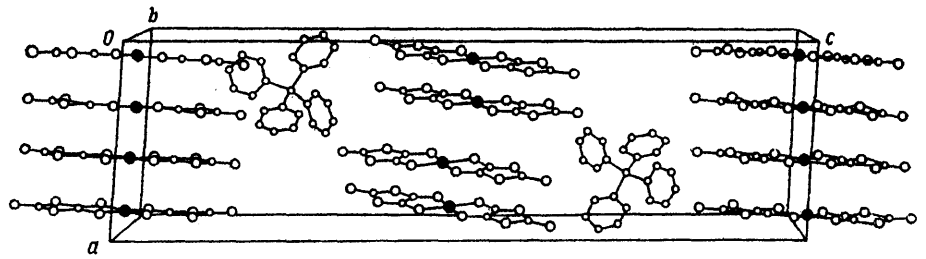


Figure 6. The crystalline structure of (VIII).[45]

(S=C)S−C distances [1.71 and 1.72(1) Å] and the C=C distance is somewhat increased [1.39(2) Å]. The anion of (VI) has an optimum planar structure and an actual optimum characteristic *mmm* symmetry. There are no characteristic structural motifs or shortened intermolecular contacts in the crystal of (VI).

Crystals of the insulator (VII) [and crystals of (XIV) which are isostructural to them] do not contain infinite structural motifs and they are composed of anions joined into dimers by (0, ½, ½) centres of symmetry (Fig. 5). In the dimers there are shortened S(1)...S(1′) contacts of 3.620(3) Å, S(1)...S(7′) contacts of 3.681(3) Å, and S(3)...S(7′) contacts of 3.605(3) Å between $[Ni(dmit)_2]^-$ anions, while in the dimers of the crystal of (XIV), where the $[Au(dmit)_2]^-$ anions are packed more closely than in the Ni analogue, these S...S contacts are 3.496, 3.491, and 3.551(3) Å. The somewhat greater degree of flattening of $[Au(dmit)_2]^-$ anions in (XIV) compared to $[Ni(dmit)_2]^-$ anions in (VII) may also be mentioned (the maximum deviation of the atoms in the anion from its mean plane is given by Δ_{max} = 0.073 and 0.102 Å respectively).

The crystal of (VIII) is composed of two independent $[Ni(dmit)_2]^{0.25-}$ anions in general positions and a Ph_4As^+ cation occupying an individual position on axis 2. The structure of the crystal of (VIII) may be described as consisting of layers of $[Ni(dmit)_2]^{0.25-}$ complexes parallel to the (001) plane, separated by layers of Ph_4As^+ cations (Fig. 6). In the anion layers stacks are formed along the $[\bar{1}10]$ direction when $z \approx 0$ and [110] direction when $z \approx ½$. The stacks consist of approximately parallel complexes grouped into tetrads (Fig. 7). The intermolecular distances in the tetrads (3.53, 3.50, and 3.53 Å) are in good agreement with the observed interplanar distance of 3.55 Å in regular stacks of the crystal of $(TTF)[Ni(dmit)_2]_2$ (XV), which is electroconductive at a low temperature.[57,58] The interplanar distance of d = 3.61 Å between the tetrads is appreciably greater than within the tetrads and is an indication of the "modulated" structure of the stacks.¶ A modulated arrangement of the planar anions in stacks also occurs in the related structures (IV) and (V)—alternation of the diads in (IV) and of the triads and tetrads in (V). Within the triads and tetrads the interplanar distances d vary from 3.48 to 3.57 Å while in the diads they are 3.44 Å. Judging by the interplanar distances, the $[Ni(dmit)_2]^{x-}$ anions interact more strongly within the diads [the crystal of (IV)] than within the triads and tetrads [crystals of (V) and (VIII)]. This is also supported by the distances between the diads, triads, and tetrads in the stacks; in (IV) the interplanar distance between diads is equal to 3.76 Å, in (V) the interplanar distance between triads is 3.53 Å and between tetrads is 3.57 Å, while in (VIII) the interplanar distance between tetrads is 3.61 Å.

¶The occurrence in the stack of two or more interplanar distances rather than one is implied.

The type of overlap of $[Ni(dmit)_2]^{0.25-}$ complexes in the tetrads of the crystal of (VIII) is shown in Fig. 8. It is clear that within the tetrads there is an appreciable relative lateral shift of the molecules, which leads to overlap of the complexes within the tetrads of the type "sulphur-over-ring" (Fig. 8*a*). Conversely, between the tetrads a longitudinal shift generally occurs, leading to overlap of the complexes of the type "metal-over-ring" (Fig. 8*b*), which may be regarded as a disturbance of the continuous structure of a stack.

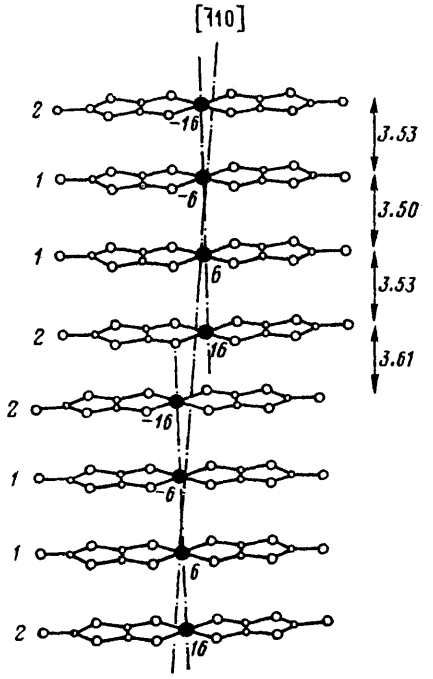


Figure 7. Projection of the anion stacks in the crystal of (VIII) on to the plane defined by the [$\bar{1}$10] vector and the long axis of the complex (the line joining the thione S atoms). The interplanar distances and magnitudes of projection of the Ni atoms from this plane ($\times 10^{-2}$ Å) are shown. The two symmetrically independent $Ni(dmit)_2$ complexes[45] are denoted by the numbers j = 1, 2.

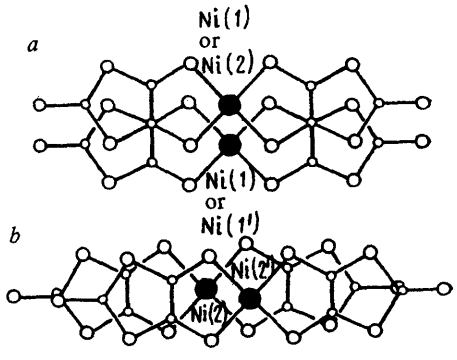


Figure 8. Intrastack overlap of $[Ni(dmit)_2]^{0.25-}$ complexes within the tetrads (*a*) and between the tetrads (*b*) of the crystal of (VIII).[45]

In the crystal of (VIII) almost all of the intermolecular S...S distances which are less than twice the van der Waals radius of the S atom (3.70 Å)[51] are contacts between stacks. If the limited disturbance to the regular stack structure (shifts of the molecules in the stacks in lateral and longitudinal directions) as mentioned above is neglected, the shortened interstack S...S contacts lead to the formation of layer motifs, parallel to the (001) plane, in the crystal of (VIII). The occurrence of these two-dimensional structural motifs governs the two-dimensional nature of the electroconductive properties of salt (VIII) [like salts (II)–(V)]. However, while the layers of Bu_4N^+ and Ph_4As^+ cations in (V), (VI), and (VIII) form "strong" barriers, virtually eliminating electrical conductivity in a "third" direction (perpendicular to the layers of $[Ni(dmit)_2]^{x-}$ anions), cations that are smaller in size, such as Et_4N^+ in (IV), also allow electrical conductivity in the third direction, resulting from the weak interaction between the terminal S atoms of neighbouring anion layers (the corresponding S...S distances are 3.90 Å). Thus, salt (IV) may be regarded as the precursor of a three-dimensional molecular metal.

It is likely that the tendency to form three-dimensional electroconductive motifs would be strengthened by replacing the Et_4N^+ cations with sulphur-containing cation-radical donor molecules.[44] In fact, in the crystal of $(TTF)_{0.5}[Ni(dmit)_2]$ the layers of $[Ni(dmit)_2]^{1/2-}$ complexes are combined with TTF molecules through S...S contacts into a quasi-three-dimensional structure.[58]

The electrical conductivity along the [010] direction of needle-shaped crystals of (VIII) is 10–15 Ω^{-1} cm^{-1}. This direction corresponds to the axis of the needles and is perpendicular to the most extensive plane of laminar crystals of (VIII). The electrical conductivity has a thermally activated nature. Low anisotropy of electrical conductivity in the (001) plane of the laminar crystal of (VIII) has been recorded ($\sigma_a : \sigma_b : \sigma_c = 1 : 1 : 10^{-5}$).

In contrast to salts (I)–(VIII), there are no anion stacks in the crystal of $(Bu_4N)[Pt(dmit)_2]$ (IX) but chains along the c axis can be distinguished, formed through interanion S...S contacts (3.55 Å). There are not enough of these contacts to form an electroconductive system; electrical conductivity along the chain is given by $\sigma_c < 10^{-8}$ Ω^{-1} cm^{-1}. The low electrical conductivity of crystals of (IX) is consistent with its IR spectrum; in the region of 400–4000 cm^{-1} there is no broad band characteristic of highly conductive molecular complexes.[46] It follows from the EPR spectra that the unpaired electrons in $[Pt(dmit)_2]^-$ anions are located on the Pt atoms.[46] Measurement of the temperature dependence of magnetic susceptibility indicates that indirect antiferromagnetic exchange through the system of these intermolecular S...S contacts occurs in the crystal of (IX).

The question of the similarity in crystal structure of the semiconductor (X) and its precursor (XI) [compound (X) is obtained by oxidation of salt (XI)], which is an insulator, is of interest. The $[Au(dmit)_2]^{x-}$ anions in crystals of (X) and (XI) retain an approximately planar structure [Δ_{max} = 0.048 Å in (X) and 0.13 Å in (XI)], the Au–S and C=C bond lengths in (X) and (XI) are similar [Au–S is 2.314–2.321(1) Å and C=C is 1.349 and 1.351(6) Å in (X) and Au–S is 2.311–2.320(2) Å and C=C is 1.345 and 1.365(9) Å in (XI)]. In (X), however, there is a difference between the (Au)S–C [1.713–1.732(4) Å] and (S=C)S–C [1.745–1.758(4) Å] distances, while in (XI) there is no such difference [1.730–1.751(7) Å and 1.725–1.747(7) Å respectively], which is a probable indication of the greater electron delocalisation in the chelate rings of complex (XI). In the crystals of both (X) and (XI) the $[Au(dmit)_2]^{x-}$ anions form stacks (with some tendency for

dimerisation to occur) along the axes a = 7.425 Å in (X) and b = 7.4186 Å in (XI) [the interplanar distances in the stacks are 3.49 and 3.79 Å in (X) and 3.57 and 3.64 Å in (XI)]. The nature of the overlap of the complexes in the stacks of crystals of (X) and (XI) varies slightly. In the crystal of (X) there is a greater relative longitudinal shift and smaller lateral shift of the anions in comparison with (XI) (Figs. 9 and 10). In (XI) there is only one slightly shortened S(5)...S(8) contact [3.681(2) Å] in the stack in contrast to the three significantly shortened S...S contacts in (X) [S(2)...S(6) at 3.489 Å, S(2)...S(8) at 3.529 Å, and S(6)...S(6) at 3.510(2) Å].

The crystal of (X) is isostructural to the crystal of (IV). As in the crystal of (IV), "dimerisation" of the anions occurs in the stacks of the crystal of (X), the interplanar distances between the planes of $[Au(dmit)_2]^{1/2-}$ anions being 3.49 and 3.79 Å. In the stacks of the crystal of (XI) each Au atom is situated at a distance of 3.620 and 3.849(2) Å from the sulphur atoms of the $[Au(dmit)_2]^-$ anions located in the same stack above and below the reference anion, and the S...Au...S vector is approximately perpendicular to the plane of the reference complex.

While the stacks of $[Au(dmit)_2]^{1/2-}$ anions in the crystal of (X) are combined into layers via a large number of shortened S...S contacts in the [100] direction (3.463–3.525 Å), the presence of twice as many Et_4N^+ cations in (XI) results in an isolated configuration of the stacks of complex anions and the structure of (XI) losing the "two-dimensional" nature that is characteristic of the crystal of (X).

The temperature dependence of the electrical conductivity of crystals of (X) has a semiconductive character. When $(Et_4N)[Au(dmit)_2]$ was oxidised, β-$\{(Et_4N)_{0.5}[Au(dmit)_2]\}$ (the β-form), which has metallic properties, was obtained in addition to the α-form.

There is definite interest in making a detailed comparison of the structures of conductive and nonconductive salts composed of uniform anions and cations but in different ratios, as in the structures of (V) and (IX) or (V) and (XII). This type of comparison is presented below for the structures of (V) and (XII), since the structural information published[46] on salt (IX) is insufficient for a detailed comparison.

On going from the electroconductive stack-layer nonstoichiometric Ni phase of (V) to the Au salt (XII), containing the same cations,

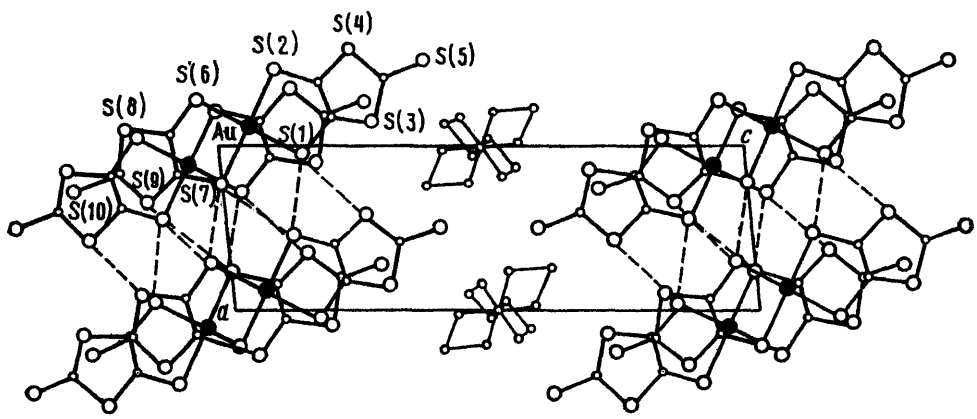


Figure 9. Projection of the crystalline structure of (X) on to the *ac* plane. The Et_4N^+ cations are randomised relative to the centres of symmetry.[47]

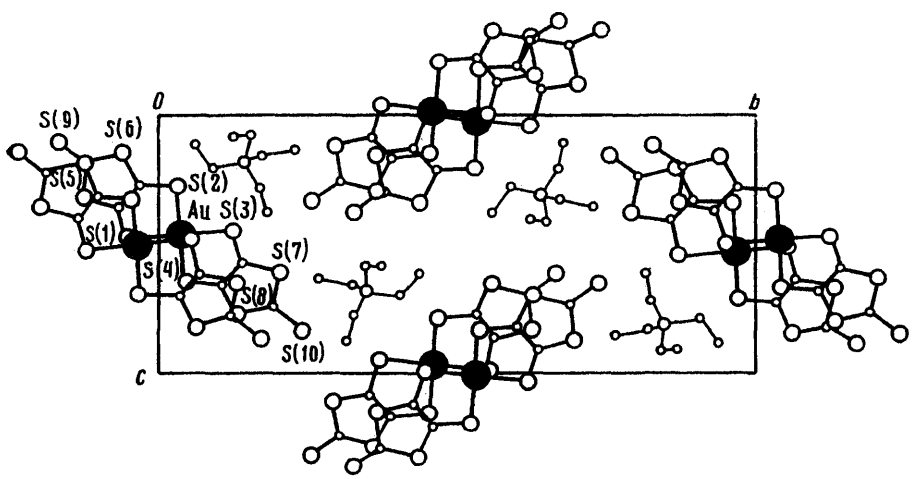


Figure 10. Projection of the crystalline structure of (XI) on to the *bc* plane.[48]

there is a more fundamental structural rearrangement than on going from (X) to (XI). A structure which is only approximately planar (in the two symmetrically independent anions Δ_{max} = 0.11 and 0.19 Å) characterises the $[Au(dmit)_2]^-$ anions of salt (XII). The Au–S distances [2.316–2.327(4) Å] in (XII) are in good agreement with those found in the two Au complexes of the type $Cat^+[Au(dmit)_2]^-$ (see Table 2). In contrast to the structure of (V), there is no conjugation in the (Au)S–C=C–S(Au) chelate residue in the crystal of (XII). The C=C, (Au)S–C, and (S=C)S–C distances in the two symmetrically independent molecules are equal to 1.29 and 1.30(2) Å, 1.73–1.76(1) Å, and 1.75–1.76(1) Å respectively.

In the crystal of (XII) the $[Au(dmit)_2]^-$ anions do not form stacks, and the symmetrically independent anions A and B which alternate along the *a* axis are not parallel, the dihedral angle between their planes being 76.2° (Fig. 11). There is only one shortened S(2)...S(8′) contact [3.565(5) Å] between the A and B anions. Between the B anions, related by (½, ½, ½) centres of symmetry, there are several shortened S(8′)...S(8″) contacts [3.495(5) Å], which form infinite chains of anions along the [011] direction. A parallel arrangement of anions A and B, in other words, the formation of stacks in the crystal of (XII), is prevented by the Bu_4N^+ cations, which are "wedged" between the anions, forming layers together with the anions parallel to the (010) plane.

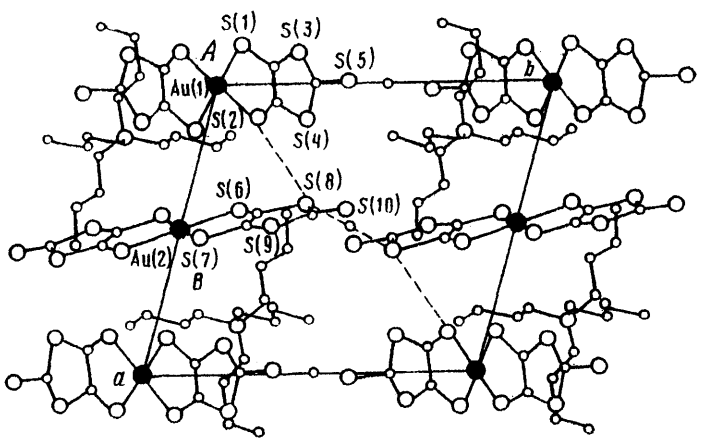


Figure 11. Projection of the crystalline structure of (XII) on to the *ab* plane.[49]

The salt $(Me_3S)[Au(dmit)_2]$ (XIII) has a structure which is quite distinct from other salts of the type $Cat_x^+[M(dmit)_2]^{x-}$ listed in Table 2. In fact, in the crystal of (XIII), which, like the crystal of (XII), is composed of two symmetrically independent anions A(1) and A(2) and cations Cat(1) and Cat(2), all anions are essentially parallel to each other (the dihedral angle between the planes of A(1) and A(2) is 1.0°) and to within about 0.1 Å occur in the same plane $(21\bar{3})$ passing through the centres of symmetry (0, ½, 0), (1, 0, ½), and (½, 1, ½) (Fig. 12). The neighbouring anion planes are separated from this plane by a distance of 3.59 Å, related to each other by the translation *a* or by centres of symmetry of the type (½, ½, ½). The Me_3S^+ cations on the edges of the layer form rows along the $[2\bar{1}1]$ direction.

At the edges of a layer in the structure of (XIII) it is possible to distinguish three types of interanion S...S contact responsible for electrical conductivity. A considerably shortened S(10)...S(10′) distance [3.128(4) Å] occurs between the A(1) anions related by a (½, 1, ½) centre of symmetry. This is the shortest intermolecular S...S distance of those found for potentially electroconductive S-containing compounds. A similar but slightly greater S...S distance (3.16 Å) occurs between stacks of planar anions in the crystal of $Li_{0.75}[Pt(C_4N_2S_2^{2-})_2].2H_2O$ ($H_2C_4N_2S_2$ is 1,2-dicyanovinylene-1,2-dithiol, σ_{293} = 30–212 Ω^{-1} cm^{-1}).[59]

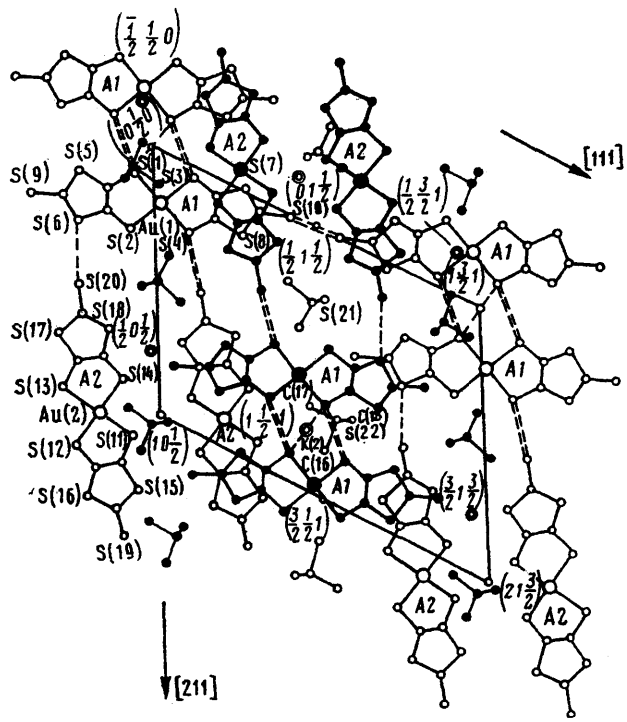


Figure 12. Projection of the crystalline structure of (XIII) on to the plane of the $[21\bar{3}]$ layer. Two layers (light and dark circles) are shown.[50]

The second group comprises shortened contacts [3.407(4) Å] between S(4)...S(19) atoms related by a (1–*x*, –*y*, 1–*z*) centre of symmetry) and S(1)...S(3) atoms [3.478(4) Å] related by a (–*x*, 1–*y*, –*z*) centre of symmetry. These contacts are appreciably less than twice the van der Waals radius of the S atom. Finally, the third group comprises contacts that are slightly less or approximately equal to twice the van der Waals radius of the S atom: S(1)...S(1), (–*x*, 1–*y*, –*z*), 3.572(4) Å; S(6)...S(20), (1 + *x*, *y*, *z*) 3.588(4) Å; and S(3)...S(5), (–*x*, 1–*y*, –*z*) 3.679(4) Å.

The layers are superimposed in such a manner that the rows of cations of each layer extending along the [211] direction occur between the rows of anions of the neighbouring layers and *vice versa* (anions between cations, Fig. 12). The shortest S...S distances between layers are nearly equal to twice the van der Waals radius of the S atom and are contacts of the type anion...cation: S(1)...S(21), (*x*, *y*, *z*), 3.654(4) Å and S(11)...S(22), (–*x*, –*y*, 1–*z*), 3.688(4) Å.

Table 3. The main data on $D[M(dmit)_2]_x$ compounds (D = donor molecule).

Compound	Chemical formula	Structural motif	M–S distance, Å	Conductivity** σ_{293}, Ω^{-1} cm^{-1}	Refs.
(XV)	$(TTF)[Ni(dmit)_2]_2$	Segregated stacks of D (d=3.65 Å) and A (d=3.55 Å)→mixed layers →quasi-three-dimensional structure	2.161–2.172 (8)	300 (metal)	[57, 58]
(XVI)	$(TSF)[Ni(dmit)_2]_3$	Stacks of A (d=3.54 and 3.63 Å)→layers of A	2.152–2.165	4 (semiconductor)	[61]
(XVII)	$(TMTSF)[Ni(dmit)_2]$	Segregated stacks of D (d=3.75 Å) and A	see*	300 (semiconductor)	[62]
(XVIII)	$(DBTTF)[Ni(dmit)_2]$	Segregated stacks of D (d=3.53 Å) and A (d=3.55 Å)	see*	300 (metal)	[63]
(XIX)	$(BEDT–TTF)[Ni(dmit)_2]$	Mixed stacks of D and A. Shortened contacts between stacks	see*	0.02 (semiconductor)	[64]
(XX)	α-$\{(BPDT–TTF)[Ni(dmit)_2]_2\}$	Segregated stacks of D and A; dimerisation of stacks of A	see*	10 (semiconductor)	[65]
(XXI)	$(TTF)[Pt(dmit)_2]_3$	Stacks of A consisting of alternating monomers and dimers→layers of A	2.29–2.32 (1)	20 (semiconductor)	[58]
(XXII)	$(HMTTeF)[Pt(dmit)_2]_{0.5}$	Tetrads of D (d=3.62 and 3.70 Å)→layers of D	see*	20 (semiconductor)	[66]

*Not in the original study.
**If the values of σ in the different crystallographic directions differ, the maximum values are given here.

The crystal of (XIII) is an insulator ($\sigma_{293} \approx 10^{-5}$ Ω^{-1} cm^{-1}). Oxidation of compound (XIII) with iodine gives a product with good conductivity ($\sigma_{293} \approx 30$ Ω^{-1} cm^{-1}), whose composition and structure have so far not been established.[50]

III. Structure of salts of 4,5-dimercapto-2-thione-1,3-dithiolates with "open" cations

A basic feature of the compounds examined in this section is the participation of both donor molecules and acceptor molecules in the formation of electroconductive corridors. We should also point out the difference between salts of "open" cations† and organic conductors of the type TTF–TCNQ[1–3] or $(TTF)[Ni(mnt)_2]$[60] (mnt = maleonitrilo-1,2-dithiolate), for example, in which the electroconductivity can in principle be related to the presence of donor stacks (in the first case) or acceptor stacks (in the second). In fact, in layers of $Cat_x^+[M(dmit)_2]^{x-}$ of the type TTF or BEDT–TTF (Table 3) both the cations of the donor and the anions of the acceptor contain a large number of sulphur atoms, which helps to increase the dimensionality of electroconductive motifs.

Crystals of $(TTF)[Ni(dmit)_2]_2$ (XV) are composed of segregated stacks of donors and acceptors extended along the [010] direction. The molecule of the donor (TTF) is completely planar while the molecule of the acceptor $Ni(dmit)_2$ is slightly bent (by 4.4°). The translation along the b axis is equal to 3.73 Å, but because both molecules—TTF and $Ni(dmit)_2$—are inclined towards the (010) plane, the intrastack interplanar distances d are less (in the donor stacks the molecules are inclined towards the (010) plane by 12° and d = 3.65 Å and in the acceptor stacks the molecules are inclined by 18° and d = 3.55 Å).

The intrastack S...S distances in the donor stacks are slightly less than in the acceptor stacks. Moreover, there are a large number of shortened intermolecular interstack S...S contacts involving molecules of both donor and acceptor in the crystal of (XV) (Fig. 13). Thus, between the $Ni(dmit)_2$ molecules of neighbouring stacks in the [001] direction there are S...S contacts (3.45 Å) which lead to the formation of a two-dimensional layer motifs of closely packed molecules of donor and acceptor located in the (100) plane. The even closer S...S contacts (3.38 Å) between the terminal S atoms of the $Ni(dmit)_2$ molecules and the TTF molecules convert the whole system of donor and acceptor molecules interacting in the crystal of (XV) into a three-dimensional arrangement. The high dimensionality of the structure assists the transition of the crystal of (XV) to a superconductive state at 1.62 K and 7 kbar.[58]

In contrast to TTF, its selenium analogue (TSF) forms a semiconductive phase of composition 1:3—$(TSF)[Ni(dmit)_2]_3$ (XVI)—with the $Ni(dmit)_2$ complex. The crystal of (XVI) is composed of two symmetrically independent $Ni(dmit)_2$ molecules (A at the centre of symmetry, B at a general position) and a TSF molecule (at the centre of symmetry). The length of the central C=C double bond in the TSF molecule is increased to 1.431 Å; this suggests that there is significant delocalisation of π-electron density in the donor molecule, which is typical for its cationic state $(TSF)^+$.[67] The lengths of the Ni–S bonds in molecules of A (2.153 and 2.165 Å) and B (2.152–2.163 Å) do not differ. In both types of anion, delocalisation of electrons occurs in the (Ni)S=C=C=S(Ni) residues; the C=C bond lengths are equal to 1.380 Å (A) and 1.380 and 1.393 Å (B), and the (Ni)S–C

†Cations of an "open" donor participate in electron transfer.

distances of 1.689 and 1.702 Å (A) and 1.688–1.708 Å (B) are appreciably less than the (S=C)S–C distances of 1.744 and 1.745 Å (A) and 1.739–1.743 Å (B).

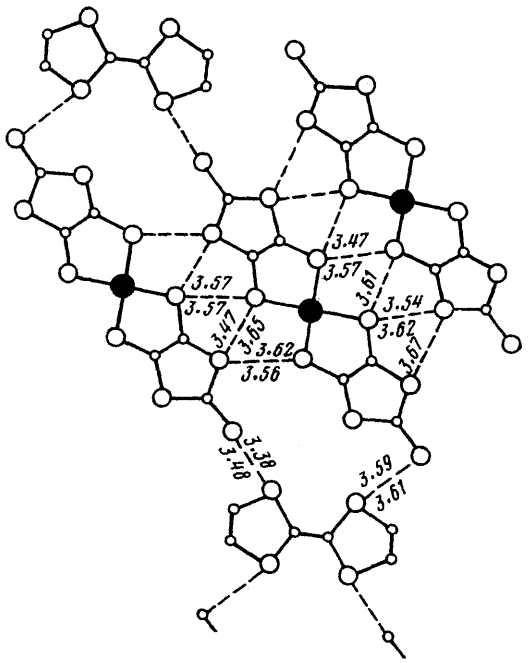


Figure 13. Part of the crystalline structure of (TTF)[Ni(dmit)$_2$]$_2$ (XV) (projection on to the *ac* plane).[57,58]

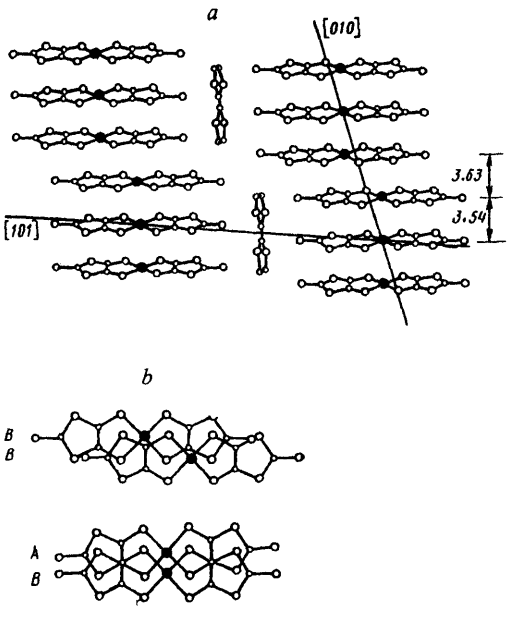


Figure 14. Crystalline structure of (TSF)[Ni(dmit)$_2$]$_3$ (XVI): *a*) relative configuration of the molecules of donor (TSF) and acceptor Ni(dmit)$_2$ (the interplanar distances in the centrosymmetric triads formed in the acceptor stacks are given); *b*) the two types of overlap of Ni(dmit)$_2$ molecules—A...B (within triads) and B...B (between triads).[61]

The Ni(dmit)$_2$ acceptor molecules are located parallel to each other with a slight shift and form BAB triads stacked along the *b* axis, with the interplanar distances within the triads equal to 3.54 Å (3.63 Å between the triads) (Fig. 14). The normal to the plane of the Ni(dmit)$_2$ complex forms an angle of 26° with the *b* axis of the crystal of (XVI). The stacks of acceptor molecules form via S...S contacts (3.503–3.646 Å) layers that are perpendicular to the [101] direction, between which are located TSF molecules not forming stacks. There are a number of shortened S...Se contacts (3.417–3.587 Å) between the terminal S atoms of the Ni(dmit)$_2$ complexes and Se atoms of the TSF molecules (sum of the van der Waals radii of S and Se atoms is 3.85 Å).[51]

When the temperature is lowered to 65 K in crystals of (XVI) a phase transition occurs, which is accompanied by a doubling of the spacing *a* and which appears to have a one-dimensional character of spin-Peierls type.[61] The shortest S...S distances occur along the *a* axis in the crystal of (XVI)—the anion stacks interact to form layers. Thus, this phase transition is probably related to dimerisation in the layers of acceptor molecules. It has been noted[61] that the spins of Ni(dmit)$_2$ complexes make a very small contribution to the total magnetic moment of the crystal of (XVI) and the total magnetic susceptibility of (XVI) is determined by TSF molecules, which have an unpaired electron that behaves as a virtually free spin, being related to the almost perpendicular relative configuration of Ni(dmit)$_2$ and TSF molecules and the large distance between TSF molecules [there are no short Se...Se contacts in the crystal of (XVI)]. On lowering the temperature (below 65 K) the spins of the TSF molecules start to line up.

A model has been proposed[56] to account for the magnetic behaviour of (XVI)—at temperatures >150 K the magnetic moment is independent of temperature and constitutes 2.1 B.M. On lowering the temperature to ~100 K the magnetic moment starts to decrease. The curve of magnetic susceptibility (χ) reaches a maximum at ~20 K, below this temperature χ decreases rapidly.

The conductive properties of crystals of (XVI) are mainly determined by the two-dimensional system of Ni(dmit)$_2$ molecules. The resistance of crystals of (XVI) along the *a* axis is very small (0.25 Ω cm) and increases monotonically on lowering the temperature.

A previous X-ray diffraction study of (TMTSF)[Ni(dmit)$_2$] (XVII) showed that the lattice of (XVII) is modulated sinusoidally. With a spacing of 9*b* on the X-ray photograph, there are satellite reflections which indicate that a ninefold superlattice occurs. The parameters of the unit cell of the superlattice are: a=15.227(4) Å, b=34.559(5) Å, c = 25.455(6) Å, β = 105.70(2)°, V = 12895(5) Å^3, Z = 18, space group $P2_1/n$. The vectors of the units cell of the fundamental lattice are given by $\mathbf{a}_0 = \mathbf{a}$, $\mathbf{b}_0 = \mathbf{b}/9$, $\mathbf{c}_0 = \mathbf{c}$. The wave amplitude of the periodic distortion of the lattice (PDL) was determined from the variation in intensities of the main and satellite reflections.

The fundamental structure of (XVII) is shown in Fig. 15. Molecules of TMTSF and Ni(dmit)$_2$ forms segregated stacks along the axis $b_0 = b/9 = 3.840$ Å. In the stacks the molecules of TMTSF donor are almost completely superimposed on each other, the interplanar distance d being equal to 3.75 Å. On the other hand, in the stacks of acceptor molecules overlap is small. The TMTSF and Ni(dmit)$_2$ molecules form a dihedral angle of 27°.

An important role in determining the direction of electron transfer is played by the anisotropy of the intermolecular overlap integrals (S) of the HOMOs of donor molecules and/or LUMOs of acceptor molecules. The transfer integral (t) is approximately proportional to S ($t \approx -ES$, where E is a constant). In accordance with the close

contacts and precise overlap of the molecules in the stacks of TMTSF, the width of the corresponding energy zone in (XVII) is twice as great as in stacks of salts of the type $(TMTSF)_2X$.[68] In the $Ni(dmit)_2$ stacks the overlap integral is very small. It has been noted[57] that the Fermi surface of the crystal of (XVII) has a flattened profile and is perpendicular to the *b* axis (the direction of the stacks). In contrast to the holes in the TMTSF stacks, the electrons in the $Ni(dmit)_2$ stacks have low mobility, which may be related to the small values of the overlap integrals along the stacks.

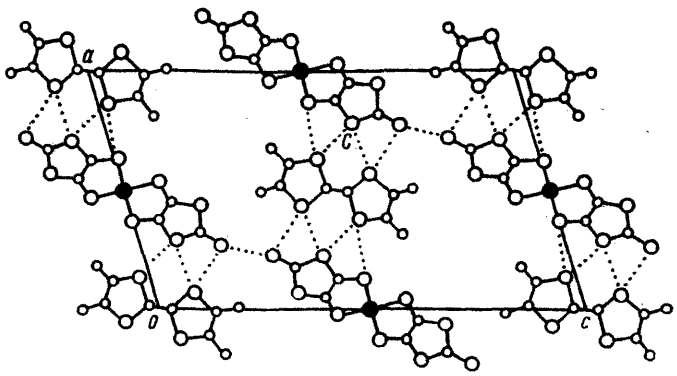


Figure 15. Projection of the main structure of (XVII) along the $\bar{b}_0$ direction. Interstack S...S contacts are shown as dotted lines.[62]

It has been noted by Kobayashi et al.[62] that when there is a planar form of the Fermi surface, if the structure is not modulated the system must be a one-dimensional metal. The observed semiconductive nature of the crystal of (XVII) is evidently due to the occurrence of PDL. It is known that a Peierls distortion with a period of $2k_F$ or PDL with a frequency of $2k_0$ can destabilise the metallic state. The existing experimental data suggest that in this case the semiconductive nature of (XVII) is due to the existence of PDL with a period of $2k_0$. Thus, in contrast to single-chain systems in which the main mechanism for disruption of stability is a Peierls distortion, destabilisation in double-chain systems with intersecting energy zones [an example of which is the crystal of (XVII)] may be caused by transverse PDL waves. The relatively large interchain interaction and large amplitude of the PDL wave are responsible for the behaviour of crystals of (XVII) as a narrow-zone semiconductor.

The structure of (XVIII) is similar to the structure of (XVII); DBTTF and $Ni(dmit)_2$ molecules form segregated stacks directed along the short axis b = 3.830(5) Å. The normals to the planes of the donor and acceptor molecules deviate in different directions from the line of the *b* axis and form angles of 23° and 22° respectively with it, namely, the cation planes are not parallel to the anion planes and intersect them at an angle of 135° (Fig. 16). The superimposition of molecules in both types of stacks occurs with a small (~1–1.5 Å) relative shift of the molecules in directions perpendicular to their long axes. In contrast to the structure of (XVII), the interplanar distances in the donor and acceptor stacks in the structure of (XVIII) are similar (3.53 and 3.55 Å), and there are no shortened intermolecular distances in the stacks of either type. Shortened contacts occur between DBTTF and $Ni(dmit)_2$ molecules that belong to neighbouring stacks along the *a* axis, which leads to a two-dimensional type of structure for (XVIII) (layers parallel to the *ab* plane). The *B*1 and *B*2 overlap integrals in the stacks (and, hence, the width of the forbidden zone) are comparable to those calculated for the system TTF–TCNQ.[69] However, in (XVIII) the ratio σ_b (within stacks): σ_a (between stacks) ≈10, i.e., less than in TTF–TCNQ, where it is ~10^2 and close to that found in $(TMTSF)_2X$ salts.[68] The overlap integrals along the *c* axis of the crystal of (XVIII) also have an appreciable value, which can suggest that there is also a significant electronic interaction in a third direction (perpendicular to the layers). For a double-chain donor-acceptor system when the interaction between frontier orbitals from different stacks is neglected, zone structures of two types are possible: with two intersecting mutually inverted dispersion curves and with "parallel" overlapping but not intersecting dispersion curves.[63] In the first case the overlap integral between the corresponding frontier orbitals of molecules in one of the stacks (S_1) has a sign opposite to that of the corresponding overlap integral (S_2) in the other stack. In the second case the signs of S_1 and S_2 are the same. Examples of systems of the first type are TTF–TCNQ[69] or (TMTSF)[Ni(dmit)$_2$] (XVII).[62] In these systems the position of the

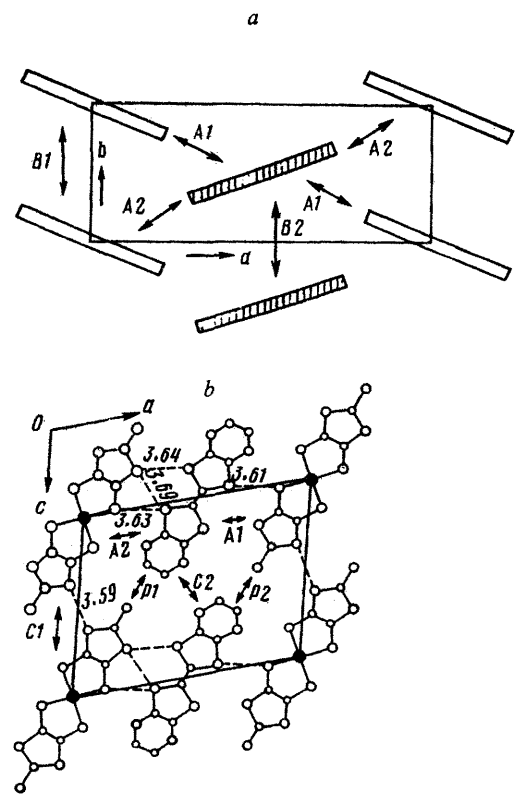


Figure 16. Crystalline structure of (DBTTF)[Ni(dmit)$_2$] (XVIII). *a*) Relative inclination of donor molecules and acceptor molecules (hatched); *b*) shortened intermolecular S...S contacts combining the donor and acceptor molecules into layers parallel to the *ab* plane. The main types of paired intermolecular interactions for which the overlap integrals of the HOMOs of the donor and LUMOs of the acceptor have been calculated are shown ($\times 10^3$): *B*1–12.72 (donor stack), *B*2–9.46 (acceptor stack), *A*1 0.875, *A*2 0.731, *C*1–0.208, *C*2 0.358, *P*1–0.307, and *P*2–0.119 (between stacks).[63]

Fermi level corresponds to the point of intersection of the dispersion curves. When the (donor–acceptor) stacks interact, the metallic state becomes unstable. The energy level that corresponds to the Fermi energy is split and a zone structure characteristic of semiconductors with a zero width of the forbidden zone is possible.[70]

In the case of the crystal of (XVIII) the overlap integrals S_1 and S_2 for the stacks of DBTTF and Ni(dmit)$_2$ respectively have the same sign. In this case the dispersion curves are "parallel". Therefore the metallic state proves stable in relation to interstack interaction. This phenomenon is responsible for the special interest in the low-temperature electrical properties of (XVIII). According to initial measurements, the electrical conductivity of (XVIII) is very high (σ_{293}, $b \approx 300\ \Omega^{-1}\ cm^{-1}$), and on lowering the temperature the value of σ_b shows very little change.

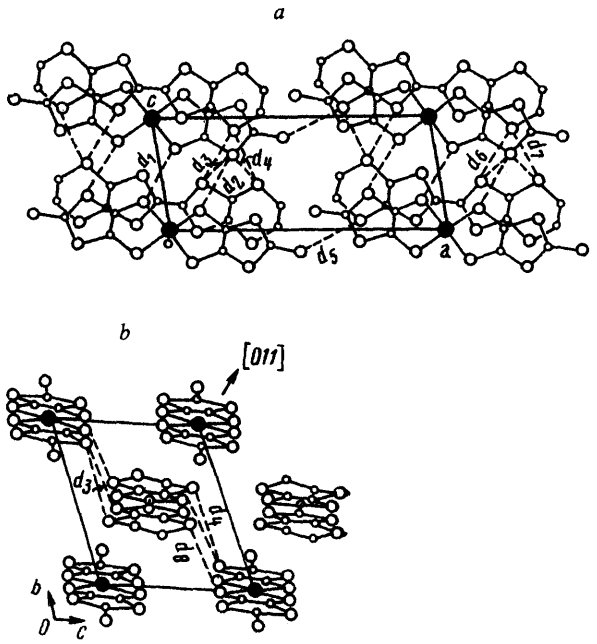


Figure 17. Crystalline structure of (BEDT–TTF)[Ni(dmit)$_2$] (XIX): *a*) projection on to the *ac* plane parallel to the plane of Ni(dmit)$_2$; *b*) projection on to the *bc* plane. The [011] direction of mixed stacks of donor and acceptor is shown. Broken lines represent the shortened interstack S...S contacts with distances d_1 = 3.53, d_2 = 3.65, d_3 = 3.65, d_4 = 3.63, d_5 = 3.58, d_6 = 3.52, d_7 = 3.41, d_8 = 3.68 Å.[64]

In contrast to the salts (XV)–(XVIII) examined above, whose structures are composed of segregated donor and acceptor stacks, in the crystal of (BEDT–TTF)[Ni(dmit)$_2$] (XIX) there are mixed stacks along the [011] direction (Fig. 17). Despite the clear overlap of cations and anions in the stacks, there are no shortened S...S contacts within the stacks probably because of the presence of the terminal ethylene spacers in the BEDT–TTF molecules. At the same time, there are quite a number of shortened S...S contacts along the [001] direction, in other words, there is a tendency which is characteristic of BEDT–TTF and M(dmit)$_2$ molecules to undergo "face" interactions.

The electrical conductivity of the crystal of (XIX) in the [001] direction at 300 K is $\sigma^{\parallel}_{300} = 0.02\ \Omega^{-1}\ cm^{-1}$ (the ratio $\sigma^{\parallel}/\sigma^{\perp} \approx 0.66$); on lowering the temperature the conductivity decreases. The energies of activation of electrical conductivity $\sigma^{\parallel}$ and $\sigma^{\perp}$ are almost equal (0.28 eV). As was noted by Kobayashi et al.,[64] all of the previously studied charge-transfer complexes (CTC) with mixed stacks were insulators, therefore the relatively high conductivity of the crystal of (XIX) caused considerable interest. Kobayashi et al.[62] have made a detailed review of physical models used to account for this phenomenon.

For a linear chain (stack) of alternating donor (D) and acceptor (A) molecules extending along the *c* axis (Fig. 18*a*) with a simple approximation of a strong bond, one-dimensional energy zones are formed by the frontier orbitals (HOMOs of the donor and LUMOs of the acceptor). It can be shown that the energy gap of such a system ($E_A - E_D$) (E_A and E_D are the energies of the LUMOs and HOMOs) is not decreased by an intermolecular interaction, and CTCs with mixed stacks are insulators. If the interaction between stacks is significantly greater than along them, molecules of D and A form segregated zones in a lateral direction (Fig. 18*b*).

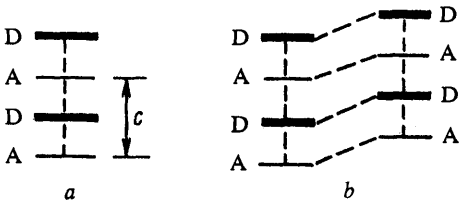


Figure 18. Two ways of arranging the molecules of donor (D) and acceptor (A) in the crystal of a CTC with mixed stacks. The direction of the main interaction between molecules of D and A is shown as a broken line.[64]

Taking into account the anisotropy of the π-orbitals, it could be assumed that the lateral intermolecular interactions in organic conductors must be small. However, calculations of the zone structure show that for molecules of the type BEDT–TTF, lateral (and/or tangential) interactions may be considerable. Calculation of the overlap integrals (*S*) of the frontier orbitals of BEDT–TTF (D) and Ni(dmit)$_2$ (A) in the crystal of (XIX) using the EH method gave the following values:[64] for contact D(x, y, z)...D(x, y, z + 1) the value of $S \times 10^3$ is 2.26, for D(x, y, z)...A(x, y, z + 1) it is 1.14, for D(x, y, z)...A(x, y, z) it is 0.75, for A(x, y, z)...A(x, y, z + 1) it is 0.28, and for D(x, y, z)...A(x + 1, y + 1, z) it is 0.11. It was noted by Kobayashi et al.[64] that since the symmetry of the HOMOs (BEDT–TTF) and LUMOs [Ni(dmit)$_2$] are different, the overlap integrals of D...A along the [011] direction in the crystal of (XIX) can be neglected. The integral of lateral overlap D(x, y, z)...D(x, y, z + 1) has the highest value, in other words, it is possible to consider segregated motifs formed by BEDT–TTF in a lateral direction relative to the stacks in the crystal of (XIX) (see also the study of Mori et al.).[71]

Kobayashi et al.[64] regard salt (XIX), which is characterised by partial D→A charge transfer and a fairly strong lateral interaction between BEDT–TTF molecules, as a novel type of organic metal, although the overlap integral (*S*) of the frontier orbitals of

BEDT–TTF molecules in (XIX) is not very large. It is known that the overlap integral of BEDT–TTF molecules is determined by the "configurational" parameters R and φ, which are governed by the relative‡ orientation of neighbouring molecules.[71] The relative orientation of BEDT–TTF molecules in the crystal of (XIX) is such that the value of S proves to be 5–10 times less than in the superconductor β-(BEDT–TTF)$_2$I$_3$.[72]

The crystal of the salt α-{(BPDT–TTF)[Ni(dmit)$_2$]$_2$} (XX), which differs from the crystal of (XIX) in its ratio of donor to acceptor and the even less planar structure of the donor molecule [because of the presence of an additional methylene group in the side rings of the molecule of (XX)], is composed of segregated stacks of donor and acceptor molecules, the acceptor stacks forming paired chains.[65] At room temperature (300 K) the electrical conductivity of (XX) is 5–10 Ω^{-1} cm^{-1} and progressively decreases as the temperature is lowered to 120 K. Below 120 K (XX) undergoes a transition to a nonconductive state. An X-ray diffraction study was carried out on salt (XX) at 293 and 96 K and no substantial differences in the structure of crystals of (XX) were detected at the different temperatures. Nevertheless, the overlap integrals of the frontier molecular orbitals, calculated for salt (XX) at 293 and 96 K, are somewhat different, which suggests that there is a strengthening of the lateral S...S interaction between the paired stacks of Ni(dmit)$_2$ in the crystal recorded at 96 K. Kobayashi et al.[65] have proposed a mechanism for the transition of (XX) to a nonconductive state, requiring only a small change in the degree of charge transfer and hence not producing significant changes in the crystalline structure of (XX) on going from 293 to 96 K.

The salt (TTF)[Pt(dmit)$_2$]$_3$ (XXI) has the same ratio of donor to acceptor as salt (XVI) (1 : 3 in both cases) and has similar parameters of its unit cell. However, it has an unusual feature which does not occur in any of the M(dmit)$_2$ salts; one of the crystallographically independent complexes Pt(dmit)$_2$ complexes forms a centrosymmetric dimer via a direct Pt–Pt bond of length 2.935 Å. Despite the formation of the Pt–Pt bond, the increase in basal Pt–S distances in the [Pt(dmit)$_2$]$_2$ dimers is small. In the dimer the Pt–S bond lengths are 2.30–2.32(1) Å, and in the monomer they are 2.29–2.30(1) Å. In the sterically less strained neutral dimer [Pt(S$_2$C$_2$H$_2$)$_2$]$_2$ the Pt–Pt distance is somewhat less (2.748 Å).[73] As in the [Pt(S$_2$C$_2$H$_2$)$_2$]$_2$ complex, the planarity of both parts of the dimer in [Pt(dmit)$_2$]$_2$ is considerably distorted, the dihedral angle between the two Pt(dmit) residues in each half of the dimer being 11.2°. The second crystallographically independent Pt(dmit)$_2$ anion remains in the crystal of (XXI) in monomer form and occupies a particular position at the centre of symmetry like the TTF molecule.

The structural motif of the crystal of (XXI) resembles that of (XVI)—layers of monomers and Pt(dmit)$_2$ dimers are parallel to the (001) plane and alternate with layers of TTF molecules. In the acceptor layers, stacks are distinguishable along the [1$\bar{1}$0] direction in which monomers and dimers alternate. The normal to the average plane of the Pt(dmit)$_2$ monomer and also the Pt–Pt bond in the dimer form similar angles (~23°) with the [1$\bar{1}$0] direction (stack axis).

‡For two molecules of BEDT–TTF which are parallel but displaced, the value of R is the relative displacement of the molecules along their long axes, and φ is the angle between the vector joining the long axes of the molecules (and that perpendicular to them) and the plane of the molecule (see, for example, Mori et al).[71]

In contrast to the crystal of (XVI), in which shortened intermolecular distances (of the type S...Se) occur only between molecules of acceptor (superimposed in stacks) and donor (located between stacks), in the crystal of (XXI) there are a considerable number of shortened S...S contacts: in the stacks within the dimers (four contacts of length 3.23–3.66 Å, inducing intramolecular contacts), in the stacks between the monomers and dimers (four contacts of length 3.63–3.66 Å), and between the Pt(dmit)$_2$ residues of monomers or dimers of neighbouring stacks (17 contacts of length 3.47–3.65 Å). On the whole the shortened S...S contacts between the acceptor molecules result in the formation in the crystal of (XXI) of the above-mentioned acceptor layers, parallel to the (001) plane. The donor molecules only participate in a single shortened intermolecular contact with the Pt(dmit)$_2$ monomer (a distance of 3.45 Å) and there are no shortened contacts of the type TTF...TTF in the crystal of (XXI).

The crystal of (XXI) is a semiconductor in the temperature range 300–100 K. The observed thermally activated electrical conductivity is probably due to the alternation of monomer and dimer molecules in the Pt(dmit)$_2$ stacks, resulting in the formation of a gap in the zone structure in the region of the Fermi level. Nevertheless, the electrical conductivity of the crystal of (XXI) at room temperature is unexpectedly high (20 Ω^{-1} cm^{-1}), which Bousseau et al.[58] thought could be due to significant interstack interaction.

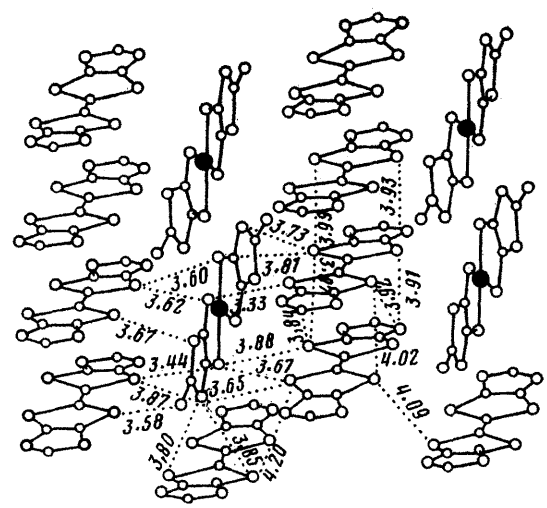


Figure 19. Short intermolecular contacts involving chalcogenide atoms in the crystal of (HMTTeF)[Pt(dmit)$_2$]$_{0.5}$ (XXII).[66]

For the crystal of (HMTTeF)[Pt(dmit)$_2$]$_{0.5}$ (XXII), the electrical conductivity at room temperature (20 Ω^{-1} cm^{-1}) and semiconductive nature of the temperature dependence of conductivity are found to be the same as for (XXI). The HMTTeF molecules are packed in the crystal of (XXII) (Fig. 19) into centrosymmetric stacks (tetrads), each with four molecules (two of them are crystallographically independent).

The interplanar distances in the tetrads are 3.62 and 3.70 Å. One of the crystallographically independent HMTTeF molecules is planar, the second is slightly bent along the line of Te...Te of one of

the heterocycles (by 9°). The tetrad stacks are combined into a two-dimensional system through short Te...Te contacts. The $Pt(dmit)_2$ complexes are located between the tetrad systems of HMTTeF molecules, the planes of the anions being approximately perpendicular to the planes of the HMTTeF molecules.

In the crystal of $(HMTTeF)_4(PF_6)_2$, the first CTC based on HMTTeF to be studied using X-ray diffraction, the HMTTeF molecules are arranged in stacks possessing a triad structure; the fourth (neutral) HMTTeF molecule is located between the stacks, with its plane parallel to the stack axis.[74] A similar structural motif also occurs in the monoclinic phase of β-$(HMTTeF)_2(PF_6)$.[66] It was noted by Kato et al.[75] that this type of packing is typical for salts with well-defined two-dimensional motifs.

The overlap integrals (S) of the HOMOs of HMTTeF molecules in the tetrads of (XXII) (-65.58×10^{-3} and 60.28×10^{-3}) are considerably higher than in other chalcogenfulvalene derivatives (for example, $S = 5\times10^{-3}$ in the TTF stacks of the salt TTF.TCNQ[69] and $S = 40\times10^{-3}$ in the TMTSF stacks of the salt (TMTSF)[Ni(dmit)$_2$] (XVII)[62]). The overlap integrals of the frontier orbitals of HMTTeF molecules of nieghbouring tetrads constitute about one third of the corresponding overlap integrals within the tetrads. The zone structure of (XXII) was calculated with a simple approximation of a strong bond.

It is difficult to determine experimentally the degree of charge transfer in salt (XXII) (from bond lengths, for example) because of the absence of accurate structural data on salts of the donor HMTTeF occurring in difference valence states.[66] If the formal charge x of the $[Pt(dmit)_2]^x$ complex is assumed to be equal to -1.0, as in the initial salt $(Bu_4N)[Pt(dmit)_2]$, the energy zone of (XXII) is 3/4 full. It follows from a calculation of the zone structure that compound (XXII) is not a metal. It is interesting that the hypothetical compound with the same composition as (XXII) but with a diad stack structure is characterised by the same form of Fermi surface as that calculated for the superconductor β-$(BEDT-TTF)_2I_3$,[76] but with a considerably wider conductivity zone than in known molecular metals,[66] which is an indication of the potentiality of the donor HMTTeF in the molecular design of low-dimensional metals.

Molecular donor-acceptor π-complexes of the type (TTF)[M(dmit)$_2$]$_x$ have all the required properties for high electrical conductivity: planarity of the donor and acceptor components, sufficiently compact and segregated stacks, substantial systems of conjugation and effective intermolecular π-overlap, and similar values of the redox potentials of donor and acceptor. Complexes of the type (TTF)[M(dmit)$_2$]$_x$ have a tendency to form two-dimensional systems, which removes the problem of Peierls distortions in one-dimensional metallic systems. This is shown particularly clearly for the compound (TTF)[Ni(dmit)$_2$]$_2$ (XV), whose high conductivity is retained down to 4 K, and at 1.6 K it undergoes a transition to a superconductive state.[76] It has been noted[56] that such behaviour of (TTF)[Pt(dmit)$_2$]$_2$ is unique for molecular donor-acceptor π-complexes that have a maximum electrical conductivity at temperatures well above 4 K (see, for example, two studies[77,78]) and is due to the presence of an extended three-dimensional network of shortened intermolecular S...S contacts in the crystal of (XV).

It was mentioned above that a distinctive feature of molecular π-complexes of the type D[M(dmit)$_2$]$_x$ (as opposed to Cat$_x$[M(dmit)$_2$] salts) is the possibility of both donor and acceptor molecules participating in the formation of electroconductive channels. In principle, by varying the molecules of donor and acceptor in the two-stack system (in which each type of stack forms its own electroconductive channel), and hence by varying the type of interaction between the stacks in layers, it is possible to obtain conductors with different properties. However, in some cases the strong interstack interaction may lead to the formation of an energy gap. In order to identify the causes of this effect, which is unfavourable for conductivity, a quantum-chemical calculation of the molecules of donor and acceptor, a study of the way in which stacks are formed and combined, and a study of the effect of the cation/anion ratio on the structure of the molecular complex are required.

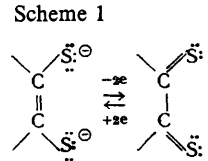
Finally, we should mention once again that D[M(dmit)$_2$]$_x$ salts (D is an open donor) have the highest conductivity among molecular solids in general and among transition metal complexes in particular. Thus, for example, the electrical conductivity of needle-shaped monocrystals of (XV) along the [010] direction (needle axis is direction of segregated stacks of donor and acceptor) is $\sigma_{293} = 300\ \Omega^{-1}\ cm^{-1}$; over the range 300–4 K the temperature dependence of electrical conductivity is of a type characteristic of metals.

IV. Crystalline structures of 5,6-dihydro-1,4-dithiin-2,3-dithiolate complexes and their salts

There is clearly a close similarity between the molecular structure of 5,6-dihydro-1,4-dithiin-2,3-dithiolates of transition metals Cat$_x$[M(DDDT)$_2$]^x (XXIII)–(XXIX) (Table 4) and BEDT–TTF (one of the most promising donors in organic conductors). The close similarity between the molecular packing in crystals of BEDT–TTF and Au(DDDT)$_2$ has also been noted.[81]

Crystals of the neutral complexes Ni(DDDT)$_2$ (XXIII) and Au(DDDT)$_2$ (XXVIII) are not isostructural. The crystal of (XXIII) is composed of two symmetrically independent centrosymmetric molecules. In both molecules the lengths of the formally double C=C bonds [1.389 and 1.388(4) Å] are considerably greater than the length of a normal C=C double bond (in cyclopentene, for example, r(C=C) = 1.323 Å),[85] approaching the length of a C⩬C aromatic bond (1.380 Å).[85] Electron delocalisation in the chelate residues (Ni)S⩬C⩬C⩬S(Ni), in the same way as in M(dmit)$_2$ complexes, may be assumed to occur in this case. It may also be assumed[36,79] that there is an approximately equal contribution of both canonical forms of the ligands (Scheme 1) to the valence state of DDDT. The average charge of each ligand is equal to -1, and the electronic configuration of the Ni atom (occurring in a formal oxidation state of 2+) is d^8.

Scheme 1



Complex (XXIII) has an essentially planar structure, the maximum deviation (Δ_{max}) of the atoms (without taking into account the peripheral C atoms of the ligands) from the plane of the central NiS_4 residue does not exceed 0.03(1) Å. Amongst the M(DDDT)$_2$ complexes in (XXIII)–(XXIX) the greatest deviation from planarity occurs in the neutral complex (XXVIII) [Δ_{max} = 0.77(1) Å]. On the whole M(DDDT)$_2$ complexes are less rigid and more likely to undergo distortion of the planar structure than M(dmit)$_2$ complexes.

In the crystal of (XXIII) two independent $Ni(DDDT)_2$ molecules are arranged in separate stacks along the short *b* translation. The angles formed by the normals to the coordination planes of the Ni atoms in the molecules of (XXIII, A) and (XXIII, B) with the *b* axis are similar (36.1 and 36.7°). The interplanar distances in the stacks of molecules (XXIII, A) and (XXIII, B) are equal to 3.78 and 3.75 Å. There are no shortened S...S contacts within the stacks. On the other hand, shortened S...S contacts occur between the stacks [3.594(3) and 3.483(3) Å].

The Ni–S distances in the $[Ni(DDDT)_2]^-$ anions of salts (XXIV) [2.146 and 2.149(2) Å] and (XXV) [2.130–2.145(9) Å] are slightly greater than in the neutral $Ni(DDDT)_2$ complex (XXIII) [2.129–2.135(1) Å]. A similar trend was noted above for complexes of the type $[M(dmit)_2]^x$. In the crystal of (XXIV) anions form layers and cations are arranged between these layers. The S...S distances in the crystal of (XXIV) are not reduced. In the crystal of (XXV) there are two types of symmetrically independent anion—(XXV, A) and (XXV, B). Anions (XXV, A) form stacks (with partial overlap of the orbitals of the anions) along the *a* axis, anions (XXV, B) are arranged roughly perpendicular to anions (XXV, A) and do not form stacks (Fig. 20). As in (XXIV), there are no shortened intermolecular S...S contacts in the structure of (XXV).

Crystals of the salt $(Bu_4N)[Ni(DDT)_2]$ (XXVI), which differs from (XXV) in that unsaturated ethylene residues occur in the DDT ligands instead of saturated residues in the DDDT ligands, are composed, in the same way as crystals of (XXV), of two symmetrically independent centrosymmetric anions (XXVI, A) and (XXVI, B). All of the atoms in the anions lie in the same plane, with the exception of the terminal C atoms of the peripheral rings. Thus, the 1,4-dithiin rings are bent along the line of S...S by 28.2° [anion (XXVI, A)] and 38.8° [anion (XXVI, B)]. Anions (XXVI, B), overlapping in a displaced manner, form stacks along the *b* axis with an interplanar distance of $d = 4.03$ Å. Anions (XXVI, A) do not form stacks, but, alternating with cations, are aligned into layers, parallel to *bc*.

Kim et al.[86] have discussed the results of an EH calculation of the coefficients of the real part of the expression for the LUMOs of the $[Ni(DDT)_2]^-$ anion, which have the same symmetry as the LUMOs of the $[Ni(dmit)_2]^-$ and $[Ni(DDDT)_2]^-$ anions.[86] In the case of the $[Ni(dmit)_2]^-$ anion, the contribution of the LUMOs localised on the "outer" $S(a_0)$ atoms constitutes about 1/5 of the contribution (a_i) of the "inner" S atoms (bonded to the Ni atom), therefore the interaction between the "terminal" molecules in crystals of $Ni(dmit)_2$ complexes is small.[87] In the $[Ni(DDDT)_2]^-$ anion there is the relationship $a_0/a_i \approx 1/2$, which must favour the formation of two-dimensional electroconductive motifs. In the $[Ni(DDT)_2]^-$ anion the relationship $a_0/a_i \approx 3/5$ is even more favourable for the formation of two-dimensional motifs; however, as has been noted,[81] in the synthesis of organic metals an important factor is the

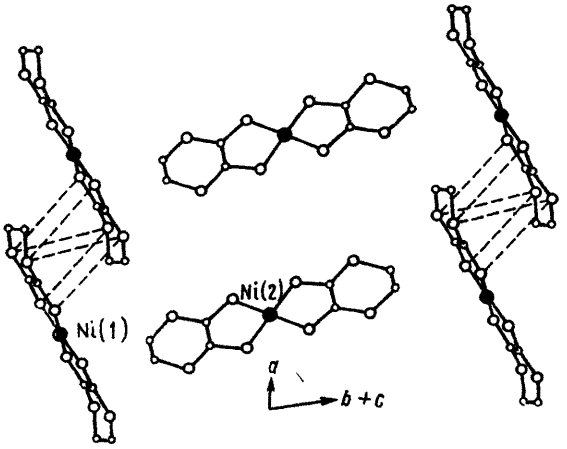


Figure 20. Packing of $[Ni(DDDT)_2]^-$ anions in the crystal of (XXV). The (XXV, A) anions [Ni(1) atom] form stacks (with partial overlap of the anions along the *a* axis). The S...S contacts in the stacks (depicted by broken lines) are not shortened. The (XXV, B) anions [Ni(2) atom] are arranged roughly perpendicular to the (XXV, A) stacks.[82]

Table 4. The main data on $[M(DDDT)_2]^x$ and $[M(DDT)_2]^x$ compounds.

Compound	Chemical formula	*x*	M–S distance, Å	Main structural motif	Conductivity σ_{293}, Ω^{-1} cm^{-1}	Refs.
(XXIII)	$Ni(DDDT)_2$	0	2.129–2.135(1)	Stacks (d = 3.75 and 3.78 Å)	10^{-5}–10^{-6}	[79, 80]
(XXIV)	$(Et_4N)[Ni(DDDT)_2]$	−1	2.146; 2.149(2)	Layers	see*	[81]
(XXV)	$(Bu_4N)[Ni(DDDT)_2]$	−1	2.130–2.145(9)	Stacks of (XXV, A) anions	see*	[82]
(XXVI)	$(Bu_4N)[Ni(DDT)_2]$	−1	2.129–2.149(10)	Stacks of (XXVI, B) anions	see*	[83]
(XXVII)	$[Ni(DDDT)_2]_3(ClO_4)_2$	2/3	2.1593–2.1720(1)	Trimers→stacks→layers	see*	[80, 84]
(XXVIII)	$Au(DDDT)_2$	0	2.280–2.317(9)	Dimers→three-dimensional structure	~10^{-4}	[82]
(XXIX)	$(Et_4N)[Au(DDDT)_2]$	−1	2.310; 2.312(3)	Not formed	10^{-5}–10^{-6}	[79]

*No accurate conductivity values.

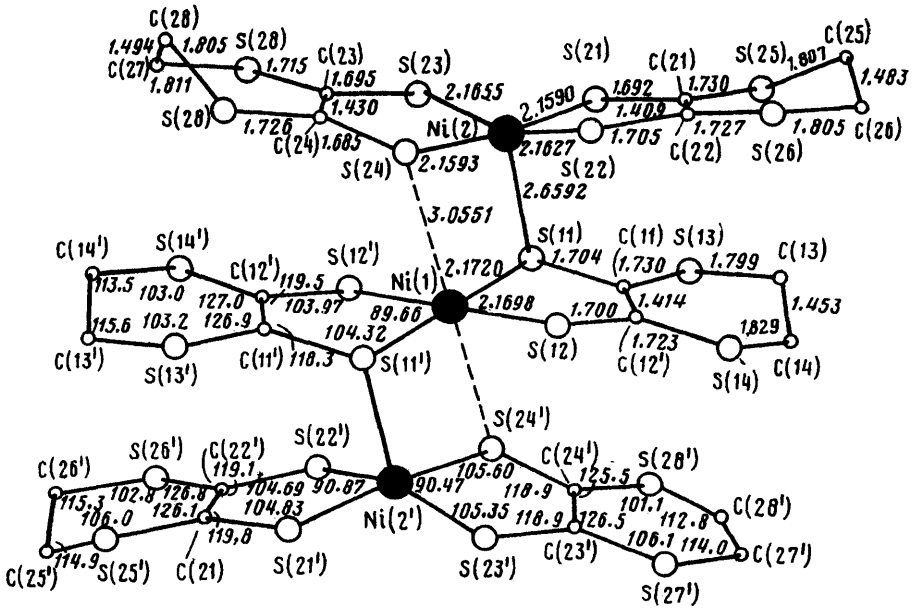


Figure 21. Structure of the trimeric $[Ni(DDDT)_2]_3^{2+}$ cation in the crystal of (XXVII).[80,84]

electrochemical properties of the components,§ namely, the magnitude of $\Delta E = E_1 - E_2$, which for the $[Ni(DDT)_2]^-$ anion has a value intermediate between ΔE for the $[Ni(dmit)_2]^-$ and $[Ni(DDDT)_2]^-$ anions.

The formal degrees of oxidation of the Ni atom and DDDT ligand in the $[Ni(DDDT)_2]^-$ complex can be represented as $[Ni^{3+}(d^7)(DDDT)_2^{2-}]^-$ or $[Ni^{2+}(d^8)(DDDT)_2^{3-}]^-$. For d^7 and d^8 configurations of the Ni atom the unpaired electron is situated on the metal atom or DDDT ligand respectively. The d^8 configuration is more consistent with a square planar coordination of the metal atom. Calculations of the population of the atomic orbitals of the Ni atom in the $[Ni(DDDT)_2]^-$ atom as well as magnetic measurements confirm a d^8 configuration of the Ni atom in this salt and that the unpaired electron is mainly located on the DDDT ligands.[82]

Salt (XXV) is paramagnetic over the whole temperature range of magnetic susceptibility measurements (from 300 to 4.2 K) in contrast to salt (XXIV), which is characterised by ferromagnetic exchange below 15 K. This difference between salts (XXIV) and (XXV) is probably due to the larger size of the cations in (XXV), which leads to an increase in intermolecular S...S distances, resulting in a weakening of magnetic exchange.[82] In fact, the shortest intermolecular S...S distances in the crystal of (XXIV) (3.98 Å within layers and 4.49 Å between layers) is appreciably less than in the crystal of (XXV) (4.75 Å within the stacks).

Electrochemical oxidation of complex (XXIII) gives salt (XXVII), the crystal of which is composed of the centrosymmetric trimeric cations $[Ni(DDDT)_2]_3^{2+}$ and two symmetrically independent ClO_4^- anions occurring in general positions. This cationic structure of the $[Ni(DDDT)_2]_3^{2+}$ complex is quite surprising. In the other crystals of (XXIII)–(XXIX) (Table 4) the $[M(DDDT)_2]^x$ complexes occur either in anionic or neutral forms. Amongst related $[M(dmit)_2]^x$ complexes that have been sufficiently well studied (in relation to the structure and electrical conductivity), again only anionic and neutral complexes are known.

The structures of the inner and outer residues of the trimeric cation of (XXVII) are considerably different. The central Ni(1) atom has a square planar coordination, increased to a [4+2]-type of pseudo-octahedral coordination through Ni(1)...S(24) and Ni(1)...S(24') interactions [3.0551(6) Å] (Fig. 21). The Ni(1)...S(24) vector forms an angle of 86.5° with the S(11)S(12)S(11')S(12') equatorial coordination plane of the Ni(1) atom. The Ni(2) atom [and symmetrically equivalent Ni(2') atom] has a fivefold tetragonal pyramidal coordination and deviates by 0.291 Å from the basal S(21)S(22)S(23)S(24) plane towards the apical S(11) atom of the inner cation residue. The basal Ni(2)–S distance [2.1590–2.1655(6) Å] is somewhat less than the equatorial Ni(1)–S distances [2.1698 and 2.1720(6) Å] and is appreciably less than the apical Ni(2)–S(11) distance [2.6592(7) Å]. All of the basal Ni–S distances in the cation of (XXVII) are clearly greater than in the neutral complex (XXIII) and anions of (XXIV) and (XXV).

The considerable similarity between the lengths of the corresponding S–C and C–C bonds in the inner and outer DDDT ligands of complex (XXVII) should be noted (Fig. 21). On the whole the lengths of the C–C bonds (average 1.418 Å) and S–C (average 1.697 Å) suggest that, as in complex (XXIII), there is appreciable delocalisation of electron density in the chelate rings and that there is an approximately equal contribution of the two canonical forms (*a*) and (*b*) (Scheme 1) to the state of the ligands of DDDT. The cation of (XXVII) can be represented as $\{[Ni^{2+}(d^8)(DDDT^-)_2][Ni^{3+}(d^7)(DDDT^-)_2]_2\}$.[80,84]

The association of dithiolene complexes through M...S interactions is well-known.[36] However, only dimeric dithiolate complexes with a coordination of the M atom of the type [4+1]

§ E_1 and E_2 are the values of the redox potentials for the reactions $[ML_2]^2 \overset{E_1}{\rightleftarrows} [ML_2]^- \overset{E_2}{\rightleftarrows} [ML_2]^0$, where ML_2 is the 1,4-dithiolene complex of the metal.[88]

were previously studied structurally.[36] Thus, the Fe atoms in the centrosymmetric dimer $\{Fe_2[S_2C_2(COOMe)_2]_4\}^{2-}$ formed through Fe...S interactions [Fe–S_{bas} distances equal to 2.230–2.256(2) Å, Fe–S_{apic} distance is 2.446(2) Å, projection of the Fe atoms from the basal planes $\Delta(Fe_{bas})$ = 0.434(1) Å, Fe...Fe is 3.120 Å] have [4+1] coordination similar to the Ni(2) atom.[89] Polymeric dithiolene complexes with a [4+2]-type of coordination of the Ni atoms (Fig. 22), like the Ni(1) atom in (XXVII), have also been theoretically predicted.[36] However, such structures have so far not been detected experimentally.

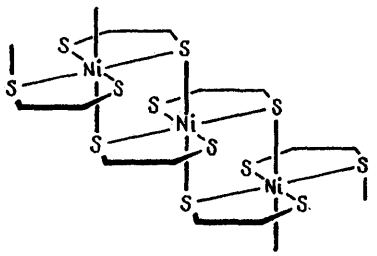


Figure 22. Hypothetical polymer chain of $Ni(edt)_2$ complexes (edt = ethylenedithiolate) combined through Ni...S interactions with [4+2] coordination of the Ni atoms.[36]

Despite the eclipsed relative configuration of the central and outer residues (Figs. 21 and 23), there is no substantial steric strain in the cation of (XXVII). The intercation contacts between the inner and outer residues [S(11)...S(23) 3.676(3) Å, S(11)...S(24′) 3.694(3) Å, S(12)...S(24′) 3.652(3) Å] are only slightly less than twice the van der Waals radius of the S atom (3.70 Å).[80] The Ni(1)...Ni(2) distance is 3.3310(4) Å, i.e., it does not correspond to a metal–metal interaction.

The cations in the crystal of (XXVII) are arranged in stacks along the axis c = 12.148 Å (Fig. 23). The S...S contacts in the stacks between the trimers are not shortened. Shortened contacts occur between stacks: $S(11)...S(25)_A$ 3.667(3) Å, $S(12)...S(21)_D$ 3.606(3) Å, $S(12)...S(26)_B$ 3.657(3) Å, $S(13)...S(25)_A$ 3.366(3) Å, $S(21)...S(24)_E$, 3.609(3) Å, $S(22)...S(23)_D$ 3.547(3) Å, $S(23)...S(26)_E$ 3.463(3) Å, $S(26)...S(27)_D$ 3.514(3) Å [atom S_A is projected from the S atom by the transformation $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, S_B by $(x, 3/2-y, \frac{1}{2}+z)$, S_E by $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, and S_D by $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$]. These shortened contacts combine the stacks of cations into layers, parallel to the *bc* plane of the crystal of (XXVII).

The molecular metal $(BEDT-TTF)_3(ClO_4)_2$ has a structure very similar to (XXVII); there are stacks along the [011] direction, in which triads of BEDT–TTF radical cations are separated with a period of 12.172 Å, short S...S contacts occurring only between stacks.[90] The low electrical conductivity of (XXVII) is probably due to the high localisation of charges in the cation trimers.

$Au(DDDT)_2$ complexes (XXVIII) are packed in the crystal with the same structural motif (centrosymmetric dimers) as for neutral BEDT–TTF molecules (Fig. 24). The similarity of structural motifs with comparable parameters of the unit cells [(XXVIII): a = 6.496(1) Å, b = 13.267(4) Å, c = 16.775(3) Å, β = 94.87(2)°, V = 1440.5(5) Å^3, Z = 4, space group $P2_1/n$; BEDT–TTF (transformed cell):[82] a = 6.614 Å, b = 13.985 Å, c = 15.721 Å,

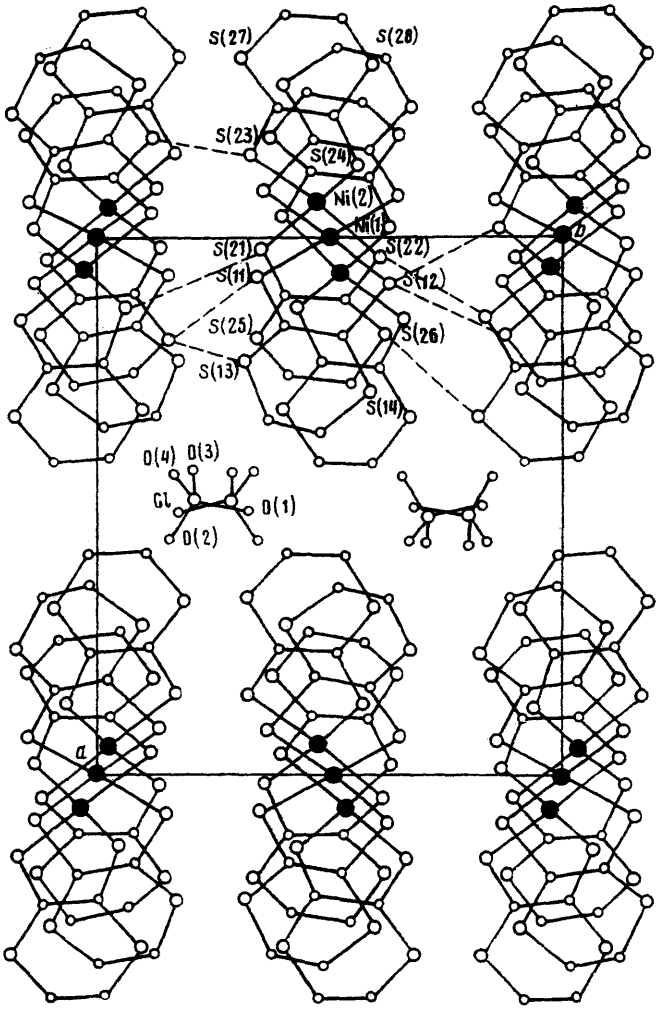


Figure 23. Projection of the crystalline structure of (XXVII) on to the *ab* plane. Shortened intercation S...S contacts are indicated by broken lines.[80,84]

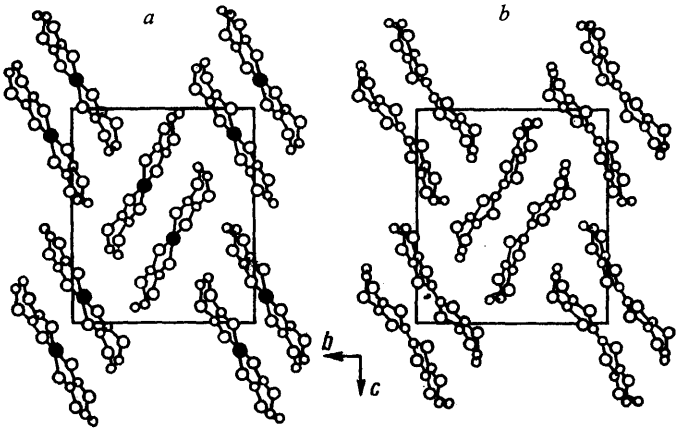


Figure 24. Projections of the crystalline structures of (XXVIII) (*a*) and BEDT–TTF (*b*) on to the *bc* plane. The diagram is taken from the study of Schultz et al.[82] and converted to the modified coordinates given by Kobayashi et al.[91]

$\beta = 93.81°$, $V = 1451$ Å^3, $Z = 4$, space group $P2_1/n$] is consistent with the structural similarity of the (XXVIII) and BEDT–TTF molecules. Shortened intermolecular S...S contacts (<3.70 Å) in both crystals only occur between dimers and combine the molecules into a three-dimensional system, and judging by the values of these contacts [the two crystals each have five shortened contacts: 3.59–3.67 Å in (XXVIII) and 3.48–3.69 Å in BEDT–TTF], the packing of the BEDT–TTF molecules is denser.

The Au–S distance in the $[Au(DDDT)_2]^-$ anion in the crystal of (XXIX) [2.310 and 2.312(3) Å (average 2.311 Å)] is slightly greater than in the neutral $Au(DDDT)_2$ complex (XXVIII) [2.280–2.317(9) Å (average 2.304 Å)] and is in good agreement with those found in $[Au(dmit)_2]^{n-}$ anionic complexes (see Table 2). It is not possible to make any definite conclusions as to whether there is electron delocalisation because of the insufficient accuracy of the X-ray diffraction study of compound (XXIX). Significant structural motifs in terms of electrical conductivity (stacks, layers) are absent and there are no shortened interanion S...S contacts.

Let us consider one more ligand system containing a tetrathioethylene unit, namely, 5,6-dihydro-1,4-dithiepin-2,3-dithiolate (DDTDT). Metal complexes obtained from it are structurally similar to the BEDT–TTF molecule. The presence of the "extra" methylene unit in this ligand (compared to the DDDT ligand) results in an even greater deviation from planarity in DDTDT ligands, namely, in a further weakening of the intrastack interaction in crystals of $[M(DDTDT)_2]^x$ complexes relative to the interstack interaction. The main data on the structure of $[M(DDTDT)_2]^x$ complexes are given in Table 5.

Table 5. The main data on the structure of $[M(DDTDT)_2]^x$ complexes.[92]

Compound	Chemical formula	x	M–S distance, Å	Main structural motif	Conductivity σ_{293}, Ω^{-1} cm^{-1}
(XXX)	$Ni(DDTDT)_2$	0	2.121, 2.138 (1)	Stacks	10^{-6}
(XXXI)	$(Et_4N)[Ni(DDTDT)_2]$	−1	2.139–2.151 (1)	Chains	10^{-5}
(XXXII)	$(Et_4N)[Cu(DDTDT)_2]$	−1	2.179–2.190 (1)	"	10^{-5}

In the crystal of (XXX) the neutral $Ni(DDTDT)_2$ complexes occupy specific positions on the 2 axes, forming stacks along the z axis ($c = 7.553$ Å). The Ni...Ni distance (3.777 Å) in a stack is too long for a metal–metal bond to be formed; there are no shortened S...S contacts in the crystal of (XXX). The central residue of complex (XXX) (excluding the C atoms of the trimethylene groups) is virtually planar ($\Delta_{max} = 0.083$ Å).

The $[Ni(DDTDT)_2]^-$ and $[Cu(DDTDT)_2]^-$ anions in the isostructural salts (XXXI) and (XXXII) have the same, almost planar structure [$\Delta_{max} = 0.088$ and 0.053 Å in the two symmetrically independent centrosymmetric anions in the crystal of (XXXI) and 0.068 and 0.072 Å in the crystal of (XXXII)]. The Ni–S distances in the $[Ni(DDTDT)_2]$ anion [2.139–2.151(1) Å] are slightly greater than in the neutral $Ni(DDTDT)_2$ complex [2.121 and 2.138(1) Å]. The anions in the crystals of (XXXI) and (XXXII) are combined into short chains along the [101] direction through short S...S contacts between the outer S atoms of the ligands [3.505 Å in (XXXI) and 3.519 Å in (XXXII)]. A stack structure does not occur in the crystals of (XXXI) and (XXXII).

V. Conclusion

By studying the structure of complexes of the type $[M(dmit)_2]^x$ and $[M(DDDT)_2]^x$ it was possible to obtain new information about the composition of low-dimensional molecular conductors. It was found at the same time that while the crystalline structure of salts of the type $(Me_4N)_{0.5}[Ni(dmit)_2]$ [(II), $\sigma = 50$ Ω^{-1} cm^{-1}] with organic cations of small size is very much like the structure of the previously known alkali metal dithiolates of the type $Li_{0.82}\{Pt[S_2C_2(CN)_2]\}\cdot 2H_2O$ with relatively good conductivity ($\sigma = 10^2$ Ω^{-1} cm^{-1},[59] fairly dense, regular, or slightly dimerised stacks of anions combined into layers), the structural motifs of crystals of $(Bu_4N)_{0.29}[Ni(dmit)_2]$ [(V), $\sigma = 1-10$ Ω^{-1} cm^{-1}, alternation of triads and tetrads in stacks of anions] and $(Ph_4As)_{0.25}[Ni(dmit)_2]$ [(VIII), $\sigma = 10-15$ Ω^{-1} cm^{-1}, tetrads in anion stacks] are very unusual. The structure of the crystal of $(Me_3S)[Au(dmit)_2]$ [(XIII), $\sigma = 10^{-5}$ Ω^{-1} cm^{-1}], which has a well-defined layer structure, the layers being formed by both anions and cations, is also unusual. It should also be noted that the structure of the anion stacks characteristic of the salts $(Me_4N)_{0.5}[Ni(dmit)_2]$ (II), $(Et_4N)_{0.5}[Ni(dmit)_2]$ (III), and α-$\{(Et_4N)_{0.5}[Au(dmit)_2]\}$ (X), which have relatively good conductivity, also occurs in their nonconductive precursors, such as in $(Et_4N)[Au(dmit)_2]$ (XI). It is true that in the latter case the stacks are not combined into layers.

Segregated stacks of donors and acceptors constitute the predominant structural motif in the highly conductive salts $D[M(dmit)_2]_x$ (D = open donor), such as $(TTF)[Ni(dmit)_2]_2$ [(XV), $\sigma = 300$ Ω^{-1} cm^{-1}], which was found previously in salts of dithiolate complexes with organic donors, such as $(C_{20}H_{12})_2\{Pt[S_2C_2(CN)_2]_2\}$, where $C_{20}H_{12}$ = perylene ($\sigma = 400$ Ω^{-1} cm^{-1})[93] and would appear to be the most conducive to a high electrical conductivity.

The structure of $(HMTTeF)[Pt(dmit)_2]_{0.5}$ [(XXII), $\sigma = 20$ Ω^{-1} cm^{-1}] is unusual. The crystal of (XXII) comprises layers of tetrads of donor molecules, the acceptor molecules being perpendicular to these layers. Quite unexpected was the comparatively high electrical conductivity of the salt (BEDT–TTF)[Ni(dmit)$_2$] [(XIX), $\sigma = 0.02$ Ω^{-1} cm^{-1}]. The crystal of (XIX) is composed of stacks with a different structure. A quantum-chemical calculation of the zone structure showed that the electrical conductivity of this salt is caused by "lateral" donor–donor (primarily) and acceptor–acceptor interactions.

Amongst these structures are to be found two forms of association of dithiolate complexes, discussed in detail by Alvarez et al.[36] In the crystal of $(TTF)[Pt(dmit)_2]_3$ [(XXI), $\sigma = 20$ Ω^{-1} cm^{-1}], one of the symmetrically independent anions participates in the formation of dimers through a direct Pt–Pt bond, whereas the second anion remains in monomer form, the acceptor stacks (combined into electroconductive layers) are composed of alternating dimers.

The second possible form of association of dithiolene complexes occurs in the crystal of $[Ni(DDDT)_2]_3(ClO_4)_2$, (XXVII), in whose trimeric dication the Ni atoms have different types of coordination. The outer atoms have a square pyramidal coordination (through a direct Ni–S bond with the inner residue), the inner atom has a pseudo-octahedral [4+2] coordination (through additional Ni...S interactions with the outer residues).

The sixfold coordination¶ of the inner Ni atom is an indication of the possible formation of infinite one-dimensional motifs of $[M(DDDT)_2]$ complexes. A further feature of the crystal of $[Ni(DDDT)_2]_3(ClO_4)_2$ is that it is essentially isostructural with the $(BEDT-TTF)_3(ClO_4)_2$ crystal, in which triads of BEDT–TTF radical cations (also arranged in stacks) act as a structural analogue of the trimeric cations (arranged in stacks). It is known that $(BEDT-TTF)_3(ClO_4)_2$ exhibits superconductive properties at very low temperatures.

Of the dithiolates discussed in this review, only crystals of $(Me_4N)_{0.5}[Ni(dmit)_2]$ (II) and $(TTF)[Ni(dmit)_2]_2$ (XV) undergo a transition to a superconductive state. Although the complex $[Ni(DDDT)_2]_3(ClO_4)_2$ (XXVII) has low electrical conductivity and is a semiconductor, its close structural similarity to $(BEDT-TTF)_3(ClO_4)_2$ gives grounds for the hope that replacement of ClO_4^- by other anions (differing from ClO_4^- in size, shape, and charge) and of Ni by another complex-forming metal (Pt, Pd, Cu) may lead to the formation of highly conductive compounds based on monomeric or polymeric $[M(DDDT)_2]^x$ complexes as donors.

On the whole, dithiolate complexes of transition metals now form an important independent class of molecular conductors (although this has much in common with purely organic conductors). There are many opportunities for modifying the structure and properties of the dithiolates. There is greatest interest in the transition from isolated monomeric dithiolates to one-dimensional and particularly two-dimensional structural motifs, namely, approaching the structures and essentially two-dimensional properties such as those of high-temperature inorganic superconductors.

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Solubility of oxygen in electrolyte solutions

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ABSTRACT. The latest advances in the study of the solubility of oxygen in water and in electrolyte solutions and of the influence of temperature and pressure on the solubility of oxygen are presented and surveyed. Advances in the development of experimental methods for the study of the solubility of oxygen are examined. The experimental results from studies of the influence of temperature and electrolyte concentration on the solubility of oxygen and their thermodynamic and molecular-statistical interpretation are described.

The bibliography includes 276 references.

Contents

I. Introduction 707
II. Methods of expressing the solubility of oxygen 708
III. Methods for the study of the solubility of oxygen 709
IV. Results of the experimental study of the solubility of oxygen in water and in electrolyte solutions 713
V. Extrema in the influence of temperature and electrolyte concentration on the solubility of oxygen 719

I. Introduction

The reviews of Konnik[1] in this journal and of Wilhelm et al.[2] in a foreign journal were published in 1977. Konnik's review[1] was devoted to the application of salting out-salting using the theories most thoroughly developed at the time (the hydration, electrostatic, and "internal pressure" theories) in relation to oxygen at 298 K. The review of Wilhelm et al.[2] contains information about the solubilities of 57 gases, including oxygen, in pure water at a pressure of 101.325 kPa and at temperatures up to 350 K. A handbook, covering the experimental data on the solubility of oxygen in water and electrolyte solutions available in the literature up to 1978, was published in 1981.[3]

A critical review,[4] containing published data on the solubility of oxygen in water (at 273–573 K) and in electrolyte solutions at 298.15 K up to the end of 1980, appeared in 1983. A bibliographic index,[5] appeared in 1984, covering 108 literature sources (published up to the end of 1983) devoted to the study of the solubility of oxygen in water and in electrolyte solutions.

During the last decade, there has been a growth of interest in the solubility of oxygen, as shown by the number of publications (more than 200) during the last ten years (1979–1988) compared with the number of publications in 1969–1978 (about 80).

The Ist International Symposium on the Problems of the Solubility of Gases was held in 1984 in Canada. It was organised by the IUPAC Commission on Solubility.[6]

The existing reviews[1,2,4] did not deal with questions concerning methods for the study of the solubility of oxygen in liquids and also questions concerning the influence of the nature and concentration of electrolytes on the solubility of oxygen over a wide range of temperatures and pressures, as well as the problem of calculating the ionic coefficients of the salting out of oxygen from aqueous solutions.

The reviews as a rule considered the range of low temperatures and pressures. Since then, considerable advances have been achieved in solving the problem of the solubility of oxygen in water and in electrolyte solutions, namely in the development of experimental methods for the determination of the solubility of oxygen and in the study of the influence of the nature and concentration of electrolytes as well as temperature on the solubility of oxygen in electrolyte solutions. These thorough studies have led to the discovery of extrema, which are manifested particularly strikingly in electrolyte solutions. The extrema involve a change in the sign of the temperature dependence of the solubility of oxygen in water and in electrolyte solutions and the corresponding change from an exothermic to an endothermic heat of solution and also a change from salting out to salting in (or conversely) with increase in the concentration of certain electrolytes. Recently, the attention of investigators has been drawn to the explanation of these phenomena on the basis of molecular-statistical and thermodynamic theories of solutions.

The extrema are of interest for many branches of engineering and chemical and biochemical technology; their discovery should give rise to new approaches to the development of rational conditions for the passivation with oxygen of steel structures in aqueous media at high temperatures and to the deoxygenation of aqueous solutions (waste, industrial, and other solutions) in order to reduce their corrosive nature and also of conditions for the electrochemical synthesis of a number of substances and other processes.

The oxygen–water system is the recommended standard system in the study of the solubility of gases in water with which one can compare the solubilities of other gases. Such comparisons are essential in the adoption of new methods, the introduction of new gas analysers.[4,7,8] The degree of saturation of water with oxygen and the chemical and biochemical consumption of oxygen are important indices of the quality of different types of water.[9]

The existing reference literature,[10] reviews,[1,2] and textbooks,[11] which are widely used in various branches of science and chemical engineering, contain erroneous data on the solubility of oxygen. This was discovered in latest careful studies.[12] In particular, this can be seen in relation to the solubility of oxygen in NH_4Cl solution.[12,13]

The aim of the present review is to give an account of advances in the study of the solubility of oxygen in aqueous solutions of pure electrolytes and their mixtures, advances in the development of experimental methods for the study of the solubility of oxygen, and

in the analysis of experimental data on the solubility of oxygen in aqueous electrolyte systems and the influence of temperature, pressure, and the nature and concentration of electrolytes on the solubility of oxygen.

Particular attention has been devoted to the extrema observed in the study of the effect of temperature and electrolyte concentration on the solubility of oxygen and to the interpretation of the results on the basis of thermodynamic and molecular-statistical theories of solutions.

II. Methods of expressing the solubility of oxygen

More than ten methods of expressing the solubility of oxygen in liquids are known:[7,14,15] the Bunsen coefficient (α), the Ostwald coefficient (L), the Kuenen coefficient (S), the absorption coefficient (β), the Cook mass absorption coefficient (C_w), the mole fraction (X_2), the constants of Henry's law (K_H, K_2, and K_c) corresponding to the three forms of its mathematical formulation, the solvomolal concentration (c_{sm}), and the solvomolal absorption coefficient (A_{sm}). In addition, the volume and weight fractions and the molar and molal concentrations are sometimes used.

The Bunsen coefficient (α) is defined as the volume V_2 (adjusted to the normal conditions T = 273.15 K and p = 101.325 kPa) of the pure gas absorbed by a unit volume V_1 of the pure solvent and measured at a temperature T and a total pressure $p_{tot} = p_1 + p_2$:

$$\alpha = (V_2/V_1)(273.15/T), \ [cm_g^3/cm_s^3],$$

where p_1 and p_2 are the partial pressures of the solvent vapour and the gas at the temperature T. The subscripts g and s referred to the gas and the solvent.

The Ostwald coefficient (L) is defined as the ratio of the absorbed volume of gas V_2, measured at the pressure p_{tot} and the experimental temperature T, to the volume of the solvent under the same conditions:

$$L = V_2/V_1, \ [cm_g^3/cm_s^3].$$

There are four ways of expressing the Ostwald coefficient:[15]

$$L_V^\circ = (V_2/V_1^\circ)_{eq},$$

where V_2 is the volume of gas absorbed by a volume V_1° of the pure liquid at p_{tot} and T;

$$L_V = (V_2/V_1)_{eq},$$

where V_2 is the volume of gas absorbed by a volume V_1 of a saturated solution at p_{tot} and T: for dilute solutions and within an error of approximately 1%, the quantities L_v° and L_V differ insignificantly;

$$L_c = (c_2^L/c_2^V)_{eq}, \quad (1)$$

where c_2^L and c_2^V are the molar concentrations of the gas in the liquid and gas phases respectively (at p_{tot} and T). This way of expressing the Ostwald coefficient was used by Ben-Naim as the most suitable for discussion of hydrophobic interaction and the thermodynamic characteristics of the transfer of gases in solutions;[16]

$$L_c^\infty = \lim_{c_2^L \to 0} (c_2^L/c_2^V)_{eq},$$

this expression is a rigorous thermodynamic definition of the coefficient L_c [see Eqn. (1)]. The formula for the relations between the four different ways of expressing the Ostwald coefficient has been published.[15]

The Kuenen coefficient (S) is defined as the volume (cm^3) of gas at a partial pressure of 101.325 kPa (adjusted to 273.15 K and 101.325 kPa) dissolved in a solution containing 1 g of the solvent:

$$S = (V_2/m)(273.15/T), \ [cm_g^3/g_s],$$

where m is the weight of the solution.

The absorption coefficient (β) is defined as the volume of gas (measured at p_{tot} = 101.325 kPa and adjusted to 273.15 K and 101.325 kPa) dissolved in a unit volume of the solvent:

$$\beta = (V_2/V_1)(273.15/T)(p_2/101.325), \ [cm_g^3/cm_s^3].$$

The Cook mass absorption coefficient (C_w) is defined as the number of moles of gas (at p_2 = 101.325 kPa) dissolved in 1 g of the solvent:

$$C_w = (V_2/m_1 V_2^\circ)(273.15/T), \ [mol/g],$$

where m_1 is the weight of the solvent and V_2° the molar volume of the gas under normal conditions.

The mole fraciton (X_2) is defined as the ratio of the number of molecules of the dissolved gas (n_2) to the sum of the numbers of molecules of the dissolved gas and the solvent (n_1):

$$X_2 = \frac{n_2}{n_2 + n_1}. \quad (2)$$

The constants of Henry's law are described by the expression

$$K_H = \lim_{X_2 \to 0} (f_2/X_2) \cong \lim_{X_2 \to 0} (p_2/X_2), \ [Pa],$$

where f_2 is the fugacity of the gas. If the gas pressure does not differ very greatly from atmospheric, we have

$$K_H = \frac{p_2}{X_2(p_2)} = \frac{1}{X_2(p_2 = 1 \text{ atm})} \ [atm].$$

The two other ways of expressing Henry's law are as follows:

$$K_2 = p_2/c_2^s,$$

$$K_c = c_2^g/c_2^s = 1/L, \ [cm_s^3/cm_g^3],$$

where c_2^g and c_2^s are the concentrations of the gas in the gas phase at a pressure p_2 and in solution respectively.

The solvomolal concentration (c_{sm}) is defined as the ratio of the number of moles of the dissolved gas to 55.51 moles of the solvent:[14]

$$c_{sm} = \alpha \cdot 55.51 \, M_1/V_2^0\rho_1 = c_m M_1 \cdot 55.51/1000 = \\ = c_M M_1 \cdot 55.51/(1000\,\rho - c_M M_2) = X_2 \cdot 55.51/(1 - X_2),$$

where α is the gas concentration (ml under normal conditions per ml of the solvent), M_1 and M_2 are the molecular weights of the solvent and the gas (g mol^{-1}), ρ_1 and ρ are the densities of the solvent and the solution (g ml^{-1}), and c_M and c_m are the molar and molal concentrations of the gas in the liquid.

The solvomolal absorption coefficient (A_{sm}) is defined as the volume of the pure gas (V_2) (at a partial gas pressure p_2 = 101.325 kPa under normal conditions) absorbed in an amount of the pure or mixed solvent such that it contains 55.51 moles of the solvent:[14]

$$A_{sm} = \alpha \times 55.51 M_1/\rho_1 = L \times 273.15 \times 55.51 M_1/T, \quad (3)$$

where ρ_1 is the density of the pure or mixed solvent. The formulae

relating the different ways of expressing the solubility of oxygen are as follows:

$$L = \alpha T/273.15, \ [cm_g^3/cm_s^3],$$
$$X_2 = (RT/Lp_2V_1 + 1)^{-1},$$
$$K_H = RT/LV_1 + p_2, \ [Pa],$$
$$K_c = 1/L, \ [cm_s^3/cm_g^3],$$
$$\alpha = S\rho, \ [cm_g^3/cm_s^3],$$
$$C_w = \alpha/V_2^\circ\rho, \ [mol/g],$$
$$L = C_wV_2^T\rho,$$
$$X_2(p_2 = 101.325 \text{ kPa}) = C_wM_1/(1 + c_wM_1),$$

where R is the gas constant, p_2 the gas partial pressure, V_1° the molar volume of the solvent at a temperature T (cm^3 mol^{-1}), ρ the density of the solution (g cm^{-3}), V_2° the molar volume of the gas in cm^3 at 0 °C, V_2^T the molar volume of the gas in cm^3 at the temperature of the measurements, and M_1 the molecular weight of the solvent (g mol^{-1}).

The expressions for the solubilities of gases become more complex if the solvent contains a dissolved electrolyte.[17] For example, Eqns. (2) and (3) assume the form of Eqns. (4) and (5) respectively:

$$X_2 = n_2 \Big/ \sum_{i=1}^{k} n_i = n_2 \Big/ \left(n_2 + n_1 + \sum_{j=3}^{k} n_j \right), \quad (4)$$

where n_1 and n_2 are the numbers of moles of the solvent and the gas respectively and n_j is the number of moles of the dissolved electrolyte;

$$A_{sm} = \alpha\,(55.51\,M_1 + c_{sm,s}M_3)/\rho = L\,(55.51\,M_1 + c_{sm,s}M_3)\,273.15/\rho T, \quad (5)$$

where $c_{sm,s}$ and ρ are the solvomolal concentration and the density of a solution of an electrolyte with a molecular weight M_3.

X_2 and K_H have been most frequently used in recent years because these quantities are more convenient for calculating the thermodynamic characteristics of the dissolution of oxygen.

The Kuenen(S) and Cook coefficients, which have the advantage of being expressed in terms of weight concentrations, i.e. temperature has no influence on the concentration, suffer from the disadvantage that, on replacement of one solvent by another, the ratio of the dissolved oxygen and the solvent changes, which makes it difficult to compare the results. The absorption (β), Bunsen (α), and Ostwald (L) coefficients depend on temperature and they can therefore be used in thermodynamic calculations only to a limited extent. The solvomolal concentration (c_{sm}) combines the advantages of the molal concentration and mole fractions, both of which are widely used in the thermodynamics of solutions. The solvomolal absorption coefficient (A_{sm}) has been recommended to characterise the solubility of gases in pure and mixed solvents.[14]

In reviews, monographs, and original papers, one may encounter a wide variety of expressions for the solubility of oxygen in liquids, which is inconvenient when they are used and compared by different workers. Therefore it was suggested in 1975[18] that the mole fraction of the dissolved gas X_2 at a pressure of 101.325 kPa and a temperature T, at which the solubility measurements were made, be used as the standard unit of the solubility of the gas.

In the study of the thermodynamics of the dissolution of oxygen in water and in other pure solvents, X_2, K_H, or c_{sm} are used.

III. Methods for the study of the solubility of oxygen

In the study of the solubility of oxygen in liquids, methods are employed which are divided in the literature by convention into physical, chemical, and physicochemical.[18–23] They are being continually improved and developed.

The volumetric and manometric methods belong to the class of physical procedures. Their essential feature involves the measurement of the volume (pressure) of oxygen absorbed by the degassed liquid or desorbed from the liquid.[2,22–28] Chemical methods are based on the interaction of oxygen with reductants.[19,22,29]

Among physicochemical methods, spectroscopic, electrochemical, chromatographic, kinetic, radiometric, and mass-spectrometric methods as well as methods based on the paramagnetic properties of oxygen (EPR, NMR) are employed. In certain methods, the dissolved oxygen is evolved from the liquid, freed from the gases and vapours present, and its amount is measured.[30,31] During the last five years, the electrochemical methods (using voltammetric membrane sensors) have been most vigorously developed. Their advantages are speed, continuity, automation, and the possibility of carrying out measurements in reaction systems, natural and industrial waters, and biological liquids.

The error of the physical methods varies from several per cent to hundredths per cent.[4,32] The error of the determination of the solubility of oxygen usually varies in the range 1–2%, rarely in the range 0.1–0.2%; an error smaller than 0.1% has been achieved.[33] The disadvantages of the physical methods include the need to use large volumes of samples, the need to degas the liquid, to carry out repeated calibrations, to monitor the purity of oxygen, and to devise large thermostats, prolonged and laborious analysis, and the impossibility of carrying out continuous measurements of the concentration of oxygen.

1. Chemical methods

Among chemical methods, the iodometric method, first introduced by Winkler who described it in its classical form,[34] has come to be most widely used. Winkler's method is based on the reaction between dissolved O_2 and $Mn(OH)_2$ in a highly alkaline medium.

On acidification in the presence of iodide, the oxidised manganese hydroxide is reduced back to manganese(II) and the iodine liberated, whose amount is equivalent to the concentration of dissolved oxygen, is determined by titration with sodium thiosulphate. The error of the determination of the concentration of dissolved oxygen in pure water by Winkler's method is 0.03–0.05 mg $litre^{-1}$ (0.5%).[19,35] Disadvantages of the method are the impossibility of determining dissolved oxygen in inorganic (NH_3, Cl_2, etc.) and organic solvents and of assessing the influence of various substances (oxidants, reductants, carbonates, phosphates, borates, and fluorides).[29,35]

It is difficult to measure continuously the solubility of oxygen by this method. Winkler's method has therefore been frequently improved and its improvement is being continued up to the present time.[36–39] A novel apparatus has been devised for saturating water with oxygen and for establishing an equilibrium between the dissolved and gaseous oxygen with subsequent application of Winkler's method.[40,41] Modifications of Winkler's method have been developed in order to eliminate the interfering influence of oxidants and reductants[29] (substances which react with I_2 and I^- [42]) in the presence of carbonates, phosphates, borates, and fluorides[40,41] and Ca^{2+}, Fe^{3+}, NO_2^-, and CH_3COO^- ions,[43] as the concentration of oxygen in coloured solutions is varied,[44] and in the presence of

high concentrations of dissolved oxygen (more than 15 mg litre^{-1}) and organic substances.[45,46] The optimum conditions for the occurrence of the chemical reactions and the principal sources of errors and the methods used to eliminate them in the determination of the solubility of oxygen by Winkler's method have been described.[29,36,37,39,47,48] The use of potentiometric and amperometric titration as well as a photometric method to determine the end point has increased the sensitivity and accuracy of the method.[19,49]

Chemical methods not involving the oxidation of manganese(II) have been described.[19] However, their accuracy is lower than that of Winkler's method, which has come to be widely used in the practical investigation of the solubility of oxygen in pure water, in electrolyte solutions, and in natural, waste, and industrial waters. Winkler's method has been recommended[4,7,35,50] as the standard method by means of which one can test and calibrate other methods and instruments.

2. Spectroscopic methods

These methods are based on the selective absorption of light by substances whose colour changes on chemical interaction with oxygen. Indigocarmine, Methylene Blue, safranine T, β-sulphoanthraquinone, diphenyl-3,4-dihydroxy-L-β-phenylalanine, 3,3'-dimethylnaphthidine, and others have been used as substances of this kind.[23] The photometric determinations[38,51] of manganese(III) compounds (after the addition of complex-forming agents), of I_3^- ions formed when Winkler's method is employed, of iron(II) complexes of 4,7-dihydroxy-1,10-phenanthroline[52] and iron(II) complexes formed with an alkaline solution of catechol,[13] of cobalt(II) complexes of L-histidine and a tetraazamacrocyclic ligand,[53] and of a cobalt(II) complex of bis(salicylaldehyde)ethylenediamine deposited on a polymer or metallic (aluminium) film[54] have been described.[38,51] Compounds containing the $[Co(MoS_4)_2]^{3-}$ ion which change colour from green to black on interaction with O_2, can serve as indicators for oxygen.[55]

Optical sensors with an emulsified oxygen indicator in a polymer layer have been developed.[56,57] The spectroscopic methods are sensitive to impurities and require the maintenance of a specified pH for a specified exposure time, as well as calibration. The advantages of the spectroscopic methods are high sensitivity and the possibility of determining very low oxygen concentrations. The range of the measured oxygen concentrations is 0.005–0.4 mg litre^{-1} and the error is 2–15%. The concentrations of oxygen in water, in electrolyte solutions,[12,13] in natural and waste waters,[58] and in organic solvents[59] have been determined by these methods. However, the spectroscopic methods have been most widely used in the determination of low oxygen concentrations in the deaerated water in large thermal power stations and atomic power stations.

3. Optical fibre sensors

During the last 3–4 years, a new type of photometric device has been developed — chemical sensors (optical sensors) which consist of a section of a fibrous light guide, on the end-face or lateral surface of which a special reagent has been deposited. The interaction of oxygen with the reagent alters its optical characteristics and leads to the appearance of a signal in the absorption, reflection, or fluorescence spectrum.[60–69] Optical sensors can be used in combination with electrochemical sensors and are promising for the determination of oxygen in various media in industrial undertakings, especially in contaminated zones dangerous to health and in clinical and biomedical research.

4. The laser absorption method

This method is based on the absorption of radiation by the molecules of the substance analysed when the frequency emitted coincides with the frequency of the absorption line.[70] The amount of radiation absorbed is governed by the number of O_2 molecules. The concentration of oxygen mixed with other gases can be determined continuously by this procedure. The sensitivity of the method is 0.003 mg litre^{-1} and the error is 1–3%.

5. Luminescence methods

These methods for the determination of dissolved oxygen are based on the glow of the phosphors formed as a result of the chemical reaction of oxygen with certain substances. Such compounds are luminol (3-aminophthalic acid hydrazide), lucigenin (bis-*N*-*N*'-methylacridinium nitrate), 9,10-diphenylanthracene, acriflavin on rigidly porous sorbents, and derivatives of 4-bromo-1-naphthol extracted into cyclodextrin and fixed on cellulose and other carriers.[71–78] The emitted intensity depends on the pH of the solution and on the presence of impurities, temperature, and exposure time. In the luminescence analysis, it is therefore necessary to stabilise all these factors. The range of the concentrations of dissolved oxygen in water measured by the chemiluminescence method in the presence of lucigenin is 6.5–15 mg litre^{-1} and the error is 0.6%. The prolonged afterglow of acriflavin on silica gel [in the oxygen concentration range $(0.3-0.5)\times10^{-3}$ mg litre^{-1}] and on cellulose [in the range 0.01–0.2 mg litre^{-1}] has been used[72] to determine microconcentrations of oxygen.

A luminescence method for the determination of oxygen with the aid of an optical fibre fluorimeter has been reported.[73] The advantages of the luminescence methods over other physicochemical methods for the determination of the concentration of dissolved oxygen are high accuracy, the possibility of using small volumes of water samples to be analysed, and the automation of the measuring process.

6. Kinetic method

This method of determining the concentration of oxygen in aqueous solutions is based on the measurement of the induction period of the reaction catalysed by the copper complex of tetrabenzo[*b*,*f*,*g*,*n*][1,5,9,13]tetraazacyclohexadecyne, in which ascorbic acid is oxidised by oxygen.[79] The range of oxygen concentrations which can be determined is 0.5–32 mg litre^{-1} with an error of 0.1 mg litre^{-1}. Compared with Winkler's method, the kinetic method yields low solubilities of oxygen. Combined luminescence-kinetic methods, based on the quenching of the luminescence of dyes by oxygen, are being developed.[80]

7. Electrochemical methods

Electrochemical methods include amperometric, potentiometric, voltammetric, coulometric, and conductimetric methods.[19,20,81] The theory of these methods has been described in detail.[19,20] The electrochemical methods for the determination of oxygen in liquids have advantages over the chemical methods.[82] Firstly, the apparatus used in electrochemical methods gives rise to an electrical output signal, which can be applied in automatic regulation and control systems. Secondly, with the aid of electrochemical methods it is possible to determine continuously the rate of change of the concentration of oxygen. Thirdly, the composition of the liquid analysed hardly changes after contact with the electrochemical sensor.

Amperometric methods are based on the measurement of the diffusion current, which varies in the course of titration. The titration is carried out at a constant potential corresponding to the region of the limiting diffusion current of oxygen. Two versions of the amperometric methods are used. In the first version, one electrode serves as the indicator electrode and the other is used as the reference electrode; in the second version, two indicator electrodes are employed (biamperometric titration).[83] The advantages of the method are high sensitivity and accuracy, high speed of measurement, and the possibility of determining oxygen in coloured and turbid aqueous and non-aqueous solutions.

Potentiometric methods are based on the dependence of the e.m.f. of a galvanic cell on the concentration of ions in the electrolyte and on the oxidation-reduction processes occurring at the electrodes as a result of the reduction of the dissolved oxygen.[84–86] The thallium electrode has been thoroughly investigated for such purposes.[87–89] The concentration of oxygen in the range 0.4–20 mg litre^{-1} with a 5% error can be determined with its aid. However, owing to the toxicity of thallium, such electrodes have not come to be widely used.

A potentiometric sensor, whose electrolytic cell consists of a reference electrode (air/Pt, Na_2HPO_4 or $NaHCO_3$), a proton-conducting solid electrolyte [$Sb_2O_3.4H_2O$, $Zr(HPO_4)_2.H_2O$, and a Nafion membrane], and a platinum indicator electrode, has been proposed.[84] It has been suggested that the Cu(II)–Cu(I)–NH_3–H_2O oxidation-reduction system be used to determine oxygen in organic and aqueous organic solvents.[85] The disadvantages of the method are the need to devise a cumbersome apparatus to maintain a definite pH.

Voltammetric methods are based on the measurements of limiting diffusion current for oxygen reduction at the cathode at a constant potential. There are two varieties of the voltammetric method: with a mercury dropping electrode and with solid electrodes. The latter are used both without membranes and with gas-permeable membranes separating the electrochemical cell from the medium in which the concentration of dissolved oxygen is measured.

The sensitivity of the classical polarographic method with respect to oxygen is 0.05–0.1 mg litre^{-1} and the error is 0.02 mg litre^{-1}. The principal disadvantages arising in the use of the mercury dropping electrode are the difficulties associated with the measurements *in situ* and the risk of contaminating the test system with mercury. Solid electrodes are free from these disadvantages. the oxygen reduction limiting current at the cathode (Pt, Au, etc.) is proportional to the concentration of dissolved oxygen.[19] Carbon glass, boron carbide, or carbon paste "wall-jet" electrodes have been described.[90] A disadvantage of the membrane-free electrodes is the possibility of their contamination. Furthermore, the medium in which oxygen is determined must exhibit a sufficient electrical conductivity, since otherwise the true current may be appreciably altered under the influence of interfering substances. These disadvantages are eliminated when membrane voltammetric sensors (MVS), first proposed by Clark,[91] are used. Platinum, palladium, rhodium, and gold cathodes are used. Instead of expensive materials, it has been suggested that the cathode by made from nickel or nichrome (however, these require additional activation)[92] as well as carbon sitals, carbon fibres, and graphite.[82,93,94] Porous silver indicator electrodes have been proposed.[95]

The use of membranes suffers from a number of disadvantages: membranes are subject to mechanical damage; if membranes are made thicker in order to increase their mechanical strength, the inertia of the sensor increases; owing to the non-uniform thickness of the membrane, a scatter of the results of measurements is observed, which requires careful calibration of the sensor; the temperature, stirring, and pH of the solution influence the readings of the sensor.[96,97] Polyethylene and fluorinated polymers 10–25 μm thick have been used as membranes.[19,98] Membranes made of a multilayer polytetrafluoroethylene film containing 60% of Mn_4N,[99] cellophane,[100] silicones,[101] and other materials[102] have been put forward.

In biologically active media, membranes are coated by a biological film, as a result of which the sensitivity of the MVS diminishes. Hydraulic or mechanical purification is normally employed. Novel sensors, in which the membrane is freed from biocontaminants by means of gases, have been developed.[103,104]

Novel stirring devices have been proposed.[105,106] In order to increase the sensitivity of the MVS, the electrodes are activated.[107–109] A sensor without a layer of electrolyte between the cathode and membrane has been developed to diminish the influence of the pressure and vibration on the membrane.[96,110] A "protecting" electrode having the same size as the cathode has been introduced to diminish the influence of the background current between the cathode and anode.[111] The range of concentrations of the sorbed oxygen measured with the aid of the MVS is 0–50 mg litre^{-1}, the relative error is 1–6%, and the sensitivity is 0.05 mg litre^{-1}.[19] MVS with pulsed action have been developed.[112–114]

Electrochemical oxygen sensors have been standardised[115,116] and have been developed to the greatest extent. They are distinguished by simplicity in operation and can be easily transported. The application of MVS makes it possible to monitor rapidly and continuously the concentration of oxygen *in situ* under industrial, laboratory, and field conditions.[117] By virtue of high speed of the response of the MVS, they are used in systems for the automatic monitoring and regulation of the oxygen conditions in the purification of sewage, in aeration devices, and for the investigation of processes involving the biochemical consumption of oxygen (BCO) and of the intensity of the respiration of microorganisms in fish-farming water reservoirs.[82,97,118,119]

In addition MVS are widely used in biology and medicine.[101,120–122] Microbial amperometric sensors for the determination of biological consumption of oxygen have been developed.[123] The interest in MVS has grown continuously.[124–138] KP-101,[139] KL-115 N20-IOA,[140] KAP-105,[141] AKVA-S,[142] KM-105, KM-101, KM-201, and KMV-110[143] oxygen measuring devices are being manufactured in the USSR. AKP-205 apparatus has been developed for the determination of low oxygen concentrations in the range 0–0.5 mg litre^{-1} subject to an error of 0.001 mg litre^{-1}.[144]

Coulometric methods are based on the direct proportionality between the weight of the electrochemically reduced oxygen and the amount of electricity which has passed through the solution. Dissolved oxygen can be determined both directly in a water sample[145] and after its evolution from the solution.[146] In these methods, there is no need to have standard samples with dissolved oxygen. During the last three years, oxygen measuring devices using an indirect coulometric method have been created.[147] An advantage of the coulometric sensors over the MVS is the smaller influence of temperature on the oxygen reduction current. The temperature-induced changes influence the reproducibility of the MVS readings owing to the temperature-induced hysteresis in the membrane. The disadvantages of these methods are the impossibility

of measuring the concentration of dissolved oxygen *in situ* and the contamination of electrodes (unless special measures are taken before analysis to purify the water). The range of variation of the oxygen concentrations which can be measured is 0.03–66 mg litre^{-1}, the relative error is ~1%, and the duration of analysis is 4–5 min.

Conductimetric methods are based on the measurement of the electrical conductivity of either an electrolyte solution in which oxygen is dissolved or of metal oxides on interaction with the gaseous oxygen evolved from the solution.[81,148–151] These methods are highly sensitive and are suitable for the continuous determination of oxygen. However, they cannot be employed to determine the concentration of oxygen *in situ* partly owing to the contamination of the electrodes. When high-frequency conductimetry is used, this problem can be solved.[19] The disadvantages of these methods are the need for preliminary passage of the sample through an ion exchanger as a result of which dissolved oxygen may be lost; when thallium oxygen-measuring devices are employed, the high toxicity of Tl^+ is a disadvantage. The range of the measureable oxygen concentrations is 0.002–1 mg litre^{-1}, the sensitivity is to within 10^{-3} mg litre^{-1}, the error is several per cent,[19] and the analysis time is several minutes. Conductimetric methods are suitable for the determination of dissolved oxygen in very pure waters with a low electrical conductivity. Analysis of the literature[81,82,87,120] of the most recent years shows that conductimetric methods are relatively unpromising.

A second type of the conductimetric determination of oxygen is based on the dependence of the electrical conductivity of metal oxides (CoO, ZnO, TiO_2, etc.) and solid electrolytes ($Nd_\alpha Y_\beta F_\gamma O_\delta$, where $\alpha = 4.5–7.5$, $\beta = 4.5–7.5$, $\gamma = 14–24$, and $\delta = 6–11$) on the concentration of oxygen and temperature.[150–152] Oxygen can be determined continuously with the aid of these procedures.

New electrochemical methods. During the last five years, new electrochemical methods have been proposed for the measurement of the concentration of dissolved oxygen: the adsorption-kinetic methods[153,154] based on the measurement of the rate of displacement of the electrode potential under the influence of dissolved oxygen, the anodic inversion, pulse, and cyclic voltammetric methods,[155–160] the chronocoulometric method,[161,162] the chronopotentiometric method,[163] the chronoamperometric method using platinum microelectrodes,[164–166] inversion potentiometric analysis,[167,168] and the method involving the measurement of the electrical resistance or the pressure exerted by the semiconducting oxide film formed on the electrode in contact with the medium being analysed.[169,170]

8. Chromatographic methods

These methods are based on the use of the difference between the adsorbabilities of oxygen, other gases, and solvent vapour.[171–175] They are used for the determination of the weight concentration of the dissolved oxygen (in a mixture of gases) in liquids.[176,177] The analysis requires 10 μl of the liquid.[172] Chromatographic methods require special equipment and calibration and with their aid it is difficult to perform continuous measurements *in situ*. The error of the method is usually 3–15%,[175] sometimes 0.33–0.5%,[172,178] the sensitivity is 0.005–0.01 mg litre^{-1},[179] and the duration of the analysis is 10–15 min, sometimes 3–5 min.[174]

A new method has been proposed[180,181] for the determination of the concentration of dissolved oxygen—liquid–gas partition chromatography based on the filtration of the sample of the analysed solution through a column with a hydrophobic filler (for example, porous polytetrafluoroethylene) and the flushing of the column with the carrier gas. In contrast to the other types of the chromatographic process, in which the stationary phase is a solid or a liquid, in this case the gas deposited on the surface of a solid carrier serves as the stationary phase. This method made it possible to automate readily the extraction of dissolved oxygen from the liquid and to reduce appreciably the lower limit of the concentrations which can be determined—to $(2–4) \times 10^{-3}$ mg litre^{-1}. In certain cases, the chromatographic procedure is combined with other analytical methods.[182,183]

9. Resonance methods

The paramagnetic properties of oxygen made it possible to develop a series of methods and to construct on their basis automatic analysers for the measurement of the concentration of oxygen dissolved in water.[21,184] The range of measured concentrations is 0–50 mg litre^{-1} and the error is 3%. An advantage of this method is the rapid response (in ~1 s) to a change in the oxygen concentration.

The EPR method is based on the use of the phenomenon of the resonance absorption of the energy of electromagnetic waves by paramagnetic species in a steady magnetic field and is used for the continuous determination of oxygen dissolved in water at concentrations in excess of 0.3 mg litre^{-1}. The error is several tens per cent. The concentration of oxygen in liquid mixtures can also be determined by this method.[185] The EPR method is promising, since, in contrast to other gases, oxygen is paramagnetic and can be determined in a mixture of gases.

The NMR method is based on the measurement of the proton spin–lattice relaxation time τ of the paramagnetic species in solution. The time τ is linearly related to the concentration of dissolved oxygen.[186] However, the application of the EPR and NMR methods requires a complex apparatus. The rate of consumption and diffusion of oxygen in cells has been investigated with the aid of NMR.[187]

10. Radiometric methods

These methods are based on the determination of the radioactivity of the elements or compounds formed when nucleons or radioactive elements react with dissolved oxygen. When a liquid sample is irradiated with fast neutrons, ^{16}O is converted into the unstable isotope ^{16}N with a half-life of 7.35 s.

The advantages of the method include a high sensitivity ($2 \times 10^{-4}–2 \times 10^{-2}$ ml litre^{-1}) and the disadvantages include the need for special equipment and calibration. In another radiometric method, the radioactive ^{204}Tl isotope is oxidised by dissolved oxygen.[188] The decrease in the intensity of the emission from ^{204}Tl is directly proportional to the concentration of dissolved oxygen. Salts dissolved in water, which influence the solubility of Tl^+ compounds, have an interfering effect. Furthermore, the extent of the oxidation of thallium depends on the pH and the presence of oxidants.

The indirect determination of the oxygen dissolved in water by atomic absorption spectrometry is based on the interaction of oxygen with thallium and the determination of Tl^+ ions by atomic absorption spectrometry. The sensitivity of the method is 0.019 mg litre^{-1} and the error is 0.04 mg litre^{-1}.[189]

11. The mass-spectrometric method

This method is used when it is necessary to know the isotopic composition of oxygen.[190–195] It is highly sensitive and does not require calibration. The relative error is 2%. A disadvantage of the method is the need for complex equipment.

An isotope-spectroscopic method for the measurement of oxygen concentration has been reported.[196] The method consists in the metered introduction of a rare stable oxygen isotope into the gas analysed, the attainment of a uniform distribution of isotopes in the resulting mixture, and the determination of the isotope composition of oxygen on the basis of emission spectra. The principle of the method is the direct proportionality of the intensity of the spectral lines or bands emitted by the atoms or molecules to their concentration in the discharge, the latter serving as the source of light. The advantages and disadvantages are the same as in the mass-spectrometric method.

The analytical possibilities for the quantitative determination of oxygen dissolved in liquids using a laser microprobe have been investigated.[197] The range of concentrations which can be measured is 0.4–2 g litre^{-1} and the error is 5%.

IV. Results of the experimental study of the solubility of oxygen in water and in electrolyte solutions

The solubility of oxygen in water and in certain electrolytes has been investigated in numerous studies whose results have been compiled and discussed.[1–4,7,198] The solubility of oxygen in pure water and sea water and also in aqueous solutions of acids, alkalis, and salts of alkali and alkaline earth metals has now been studied most fully.[1,4,198]

1. Solubility of oxygen in water at different temperatures

In most studies, the solubility of oxygen in water was investigated in the temperature range 273–348 K at atmospheric pressure. With increase in temperature, the vapour pressure of water increases and it is more difficult to maintain a constant degree of saturation. This entails a decrease in the accuracy of the determination of the experimental solubilities of oxygen. Therefore it has been suggested that the oxygen solubility data[4] be expressed with different errors in two temperature ranges: with an average error of 0.30% at temperatures below 348 K and with an average error of 2% above 348 K. The International Standard ISO 5814-84 lists the solubilities of oxygen in water as a function of temperature (0–40%) and salinity (0–35 g dm^{-3}).[35]

In most studies, the gas used to saturate the solution with oxygen was air and the experimental solubilities of oxygen were adjusted to p_{O_2} = 101.325 kPa taking into account the vapour pressure of water. The use of air instead of pure oxygen is a disadvantage, since, together with oxygen, nitrogen and other gases (nitrogen, carbon and sulphur oxides as well as ammonia) dissolve and interact with water, which may alter the chemical compositions of the solutions and their pH. This factor has not been taken into account in all studies and special measures to purify the air saturating the solutions have not always not been taken. Therefore the studies in which pure oxygen was used to saturate the solutions are the most reliable and accurate. Furthermore, the air or oxygen supplied to the solution must be saturated with water vapour and at elevated temperatures must be heated. Such improvements of the methods have been described.[40,41]

Battino et al.[4] treated by least squares the most reliable experimental data from 15 literature sources in the range 273–348 K and obtained the following expression:

$$\ln X_2 = -64.21517 + 8391.236/T + 23.24323 \ln(T/100). \quad (6)$$

(average error 0.30%), where X_2 is the solubility (mole fractions) of oxygen in pure water and T is the temperature (in K).

Benson et al.[193] proposed the following equation for the description of the temperature dependence of the solubility of oxygen in water in the range 273–373 K:

$$-\ln X_2 = 3.71814 + 5.59617 \cdot 10^3/T - 1.049668 \cdot 10^6/T^2, \quad (7)$$

with an average error of 0.017%.

The solubilities of oxygen in water at 273–373 K, calculated[4] from Eqns. (6) and (7) are presented in Table 1.

The differences between the solubilities of oxygen in water which we calculated by Eqns. (6) and (7) are presented in Fig. 1 as a function of temperature. At temperatures below 323 K, the relative difference of the solubilities is 0.2–0.4%, which agrees with the error (0.3%) of the calculation of the solubility of oxygen by Eqn. (6). At temperatures above 328 K, greater discrepancies between the solubilities of oxygen calculated by the two formulae are observed. This shows that the representation of the oxygen solubility data in the two temperature ranges (273–348 and 348–573 K) proposed by Battino et al.[4] is not altogether correct. It is desirable to restrict the first range to 273–328 K. In this range, the average error of the solubility of oxygen in water does not exceed 0.30%.

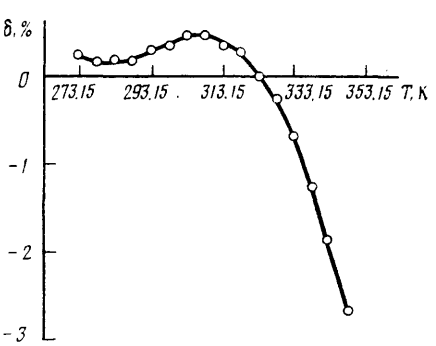


Figure 1. Temperature dependence of the relative difference δ between the solubilities of oxygen in pure water calculated by Eqns. (6) and (7).

The solubility of oxygen in water above 343 K has been studied in a number of investigations.[199–202] The following equation has been obtained[203] on the basis of experimental data:[199,204]

$$\ln X_2 = -54.0411 + 6889.61/T + 18.554 \ln(T/100). \quad (8)$$

The solubilities of oxygen in water at 348–573 K, calculated by Eqn. (8), are also listed in Table 1. The error of the determination of these quantities is 2%.

Table 1. The solubilities of oxygen ($10^5 X_2$, mole fraction) in water at 273.15–573.15 K (p_{O_2} = 101.325 kPa).[4,193,203]

T, K	From Eqn. (6)	From Eqn. (7)	T, K	From Eqn. (6)	From Eqn. (7)	T, K	From Eqn. (8)	T, K	From Eqn. (8)
273.15	3.949	3.958	313.15	1.867	1.874	353.15	1.478	453.15	2.038
278.15	3.460	3.465	318.15	1.773	1.778	358.15	1.462	473.15	2.388
283.15	3.070	3.075	323.15	1.697	1.697	363.15	1.450	493.15	2.852
288.15	2.756	2.761	328.15	1.635	1.631	368.15	1.445	513.15	3.460
293.15	2.501	2.508	333.15	1.586	1.575	373.15	1.444	533.15	4.250
298.15	2.293	2.301	338.15	1.549	1.530	393.15	1.487	553.15	5.276
303.15	2.122	1.982	343.15	1.521	1.493	413.15	1.599	573.15	6.603
308.15	1.982	1.991	348.15	1.502	1.463	433.15	1.780		

The solubility of oxygen in heavy water (D_2O) has been measured as a function of temperature[205] (p_{O_2} = 101.325 kPa):

T, K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$10^5 X_2$, mole fraction	3.729	3.332	2.950	2.673	2.459	2.263	2.101	2.000

The solubility of oxygen in D_2O is higher than in H_2O, but the difference diminishes with increase in temperature from 278 to 313 K.

The solubilities of different oxygen isotopes in pure water[193,194] and sea water[195] have been investigated. Heavy oxygen isotopes dissolve in water more readily than the light isotopes.

2. Minima in the temperature variation of the solubility of oxygen in water

Table 1 shows that, with increase in temperature, the solubility of oxygen diminishes to a minimum and then increases. The minimum solubility of oxygen in pure water is observed at 373 K (p_{O_2} = 101.325 kPa) and is independent of whether the water was saturated with air or oxygen.

The minima on the curves relating the solubility of gases in liquids to temperature were first observed in the study of the solubilities of hydrogen[206] and helium[207] in water. On the basis of the general rules governing the behaviour of binary mixtures, it has been pointed out[208] that there must be a minimum in the temperature variation of the solubilities of all gases in liquids.

The presence of a minimum in the temperature variations of the solubilities of gases and the thermodynamic interpretation of this phenomenon have been reported.[209] A minimum has been observed experimentally[210] in the temperature variation of the solubility of radon in water (at T_{min} = 366 K). However, the author himself[210] believed that the minimum in the solubility of radon is an anomalous phenomenon. It has been reported[211] that the minimum in the solubilities of the majority of gases in water occurs in the range 323–343 K. The minimum solubility of oxygen in water at T_{min} = 348 K (p_{O_2} = 10 MPa) has been established experimentally.[212,213] Later the inversion in the influence of temperature on the solubility of oxygen in water was confirmed,[199,200] but the values of T_{min} were found to be higher than those observed previously[212,213] by 37 K (at p_{O_2} = 7–35 atm and 70–140 atm). A minimum has been observed[214] in the influence of temperature on the solubility of oxygen in pure water at approximately 373 K (p_{O_2} = 20–60 atm). The latest studies[201,215] established the presence of a minimum in the solubility of oxygen in water at ~373 K regardless of pressure (in the range 1–5 MPa). An increase in pressure from 0.7 to 5 MPa hardly affects T_{min},[199,201] but a further increase in pressure from 7 to 10 MPa leads to a decrease in T_{min}.[216] The presence of a minimum in the plot of the solubility of oxygen in water against temperature is a firmly established fact. The explanation of this phenomenon is considered below.

3. Solubility of oxygen in water—a recommended standard in the measurements of the solubilities of gases in liquids

The solubility of oxygen in pure water at 298.15 K has been more often and more thoroughly measured than in other gas–liquid systems. After a critical analysis of the most reliable data, Battino and Clever[7] recommended as a standard the solubility of oxygen in pure water at 298.15 K and p_{O_2} = 101.325 kPa, which is characterised by the following parameters: α = 0.02847, L = 0.03108, $X_2 = 2.295 \times 10^{-5}$, and $c_w = 1.274 \times 10^{-6}$.[7] The average error in the calculation of this solubility from seven of the most reliable results is 0.21%.

Numerous data obtained by different workers for the solubility of oxygen in water over a wide temperature range have been analysed[4] and the solubilities in the range 273.15–348.15 K have been recommended with an average error of 0.30% (Table 1). The solubility of oxygen in water, amounting to $X_2 = 2.301 \times 10^{-5}$ (T = 298.15 K; p_{O_2} = 101.325 kPa, was determined in 1979 with an average error of 0.017%.[193] This solubility is greater by 0.35% than the value $X_2 = 2.295 \times 10^{-5}$ recommended by Battino and Clever.[7] The error in the measurement of the solubility of oxygen obtained by Benson et al.[193] is smaller by an order of magnitude than that of the value recommended by Battino and Clever.[7] Therefore the quantity $X_2 = 2.301 \times 10^{-5}$ may be regarded as the most reliable and the solubilities of oxygen obtained by new methods, with the aid of new types of apparatus, etc. should be compared with it.

4. The influence of the nature and concentration of electrolytes on the solubility of oxygen in water

The introduction of electrolytes into water leads as a rule to the salting out of oxygen.[40,198,217] The salting out coefficient, called in the literature the Sechenov coefficient $K_{c\alpha}$, has come to be regarded as a quantitative characteristic of this phenomenon:

$$K_{c\alpha} = 1/c \lg(\alpha_0/\alpha), \text{ [litre mol}^{-1}\text{]}, \quad (9)$$

where c is the molar concentration of the electrolyte and α_0 and α are the solubilities (expressed in terms of the Bunsen coefficients) of oxygen in pure water and in the electrolyte solution. Over a narrow range of electrolyte concentrations and for low values of the latter, Eqn. (9) holds rigorously. This concentration range depends on the nature of the electrolyte and the gas.[1,40,218–220] There exist numerous modifications of the Sechenov equation.[219,221,222] It has been shown[221] that for appreciable electrolyte concentrations it is useful to formulate Eqn. (9) as follows:

$$K_I = 1/I \lg(\alpha_0/\alpha), \text{ [litre mol}^{-1}\text{]}, \quad (10)$$

where the molar concentration of the electrolyte c has been replaced by the ionic strength I:

$$I = 1/2\sum c_i Z_i^2, \text{ [litre mol}^{-1}\text{]},$$

where c_i is the molar concentration of the ith ion and Z_i is its charge. Eqn. (10) holds for $I \leqslant 5.6$.[223]

It has been proposed[218,219] that the dependence of the logarithm of the solubility of oxygen on the electrolyte concentration over a wide range of the latter be described by the formula

$$\lg(\alpha_0/\alpha) = K_c^0 c/(1 + K_c' c), \quad (11)$$

where K_c^0 and K_c' are constants. For $c \to 0$, Eqn. (11) is converted into the Sechenov equation (9). The available literature values of the coefficients for the salting out of oxygen from solutions in 70 electrolytes, calculated with the aid of Eqn. (9) over a wide range of experimental conditions, have been compiled and tabulated.[220] In one of the latest studies,[13] the coefficients for the salting out of oxygen from solutions of 68 electrolytes at 310.2 K and p_{O_2} = 101.325 kPa were determined. In some communications, there is no information about the determination of the particular equilibrium concentration (solubility) of oxygen and the errors of the calculation of the salting out coefficients are not indicated. The corresponding data are not considered in this review. The oxygen salting out coefficients depend on the nature of the anions and cations, temperature and pressure, and for certain electrolytes also on their concentration.

(a) Solutions of acids

Coefficients for the salting out of oxygen from aqueous HCl, H_2SO_4, and HNO_3 solutions are presented in Table 2. The solubility of oxygen as a function of H_2SO_4 concentration is described by a curve with a maximum.[224] The oxygen salting out coefficients decrease with increase in the H_2SO_4 concentration.[224] An appreciable effect of pressure (in the range 0.5–1.5 MPa) on K_c has not been observed.[228] The coefficient for the salting out of oxygen from 1 M H_2SO_4 is 0.10 litre mol^{-1} (p = 5 MPa) at 323 K and hardly changes with increase in temperature to 523 K.[225] Extrema are observed in the dependence of the solubility of oxygen on the HNO_3 concentration and temperature. This will be described in detail below.

The dependence of the logarithm of the solubility of oxygen on the H_3PO_4 concentration (in the range 1.5–14.6 M) at 298–333 K is not linear.[229] The literature data[166,230,231] concerning the influence of the H_3PO_4 concentration (85–100 wt.%) and temperature (373–423 K) on the solubility of oxygen are contradictory.

Table 2. The coefficients of the salting out of oxygen from 1.0 M HCl, H_2SO_4, and HNO_3 solutions.

Acid	T, K	p_{O_2}, MPa	$K_{c\alpha}$, litre mol^{-1}	Refs.
HCl	288.15	0.1	0.044	[224]
	298.15	0.1	0.031	[224]
	310.2	0.1	0.027	[13]
H_2SO_4	288.15	0.1	0.105	[224]
	298.15	0.1	0.087	[224]
	323.15	5	0.10	[225]
HNO_3	283.15	1–6	0.0440	[226, 227]
	293.15	1–6	0.0255	[226, 227]
	303.15	1–6	0.0175	[226, 227]
	310.2	0.1	0.010±0.004	[13]
	313.15	1–6	0.0115	[226, 227]
	323.15	1–6	0.0090	[226, 227]
	333.15	1–6	0.0050	[226, 227]

Table 3. The coefficients of the salting out ($k_{c\alpha}$) of oxygen from solutions of alkalis (p_{O_2} = 101.325 kPa).

Alkali	298.15 K [40]		310.2 K [13]	
	c^*, M	$K_{c\alpha}$, litre mol^{-1}	c^*, M	$K_{c\alpha}$, litre mol^{-1}
LiOH	0–0.07	0.332	0–4.058	0.137
LiOH	0.15–1.2	0.091	—	—
NaOH	0–1.2	0.181	0–4.071	0.169
KOH	0–0.8	0.176	0–4.871	0.160
RbOH	0–0.5	0.168	0–3.187	0.161
CsOH	0–0.5	0.158	0–2.325	0.153

* c is the range of concentrations of alkalis for which $K_{c\alpha}$ has been determined.

Note. The numerals in square brackets denote references (Translator).

(b) Solutions of alkalis

The coefficients for the salting out of oxygen from solutions of alkali are presented in Table 3, which shows that two different values of $K_{c\alpha}$ are observed in LiOH solutions at 298.15 K: in the region of low (up to 0.07 M) and high (0.15–1.2 M) electrolyte concentrations. A similar effect has been established in a study of the solubility of oxygen in NaOH solutions at 323–423 K and p_{O_2} = 1–5 MPa:[232] an anomalously large oxygen salting out coefficient has been observed in 0.01–0.1 M NaOH solutions (K_c =

0.65 litre mol^{-1}). An increase in temperature from 323 to 523 K (p_{O_2} = 5 MPa) hardly affects K_c in NaOH solutions.[225] At 310.2 K, the quantity $K_{c\alpha}$ is constant over the entire concentration range (0–4.059 M) of LiOH.[13] The dependence of the solubility of oxygen on the KOH concentration is described satisfactorily by the Sechenov equation (9) over a wide range of concentrations (0–16 M) and temperatures (288–373 K).[229,233–235]

The coefficient for the salting out of oxygen from NH_4OH solution is very low (k_c = 0.006 litre mol^{-1}) and hardly changes with increase in the NH_4OH concentration (0–8 M) and temperature (323–423 K).[225]

(c) Salt solutions

Salts as a rule salt out oxygen from solutions (Tables 4–6). It is seen from Tables 4–6 that the oxygen salting out coefficients as a rule increase with decrease in the atomic number and size of the ion. For salts with the F^-, BO_2^-, and $B_4O_7^{2-}$ ions, anomalously large values of K_c have been observed.[220] Salts with H^+, NH_4^+, and Li^+ cations are exceptions (Table 6).

Table 4. The coefficients K_c (litre mol^{-1}) of the salting out of oxygen from solutions of alkali metal halide salts (T = 298.15 K, p_{O_2} = 0.1 MPa).[40]

Ion	F^-	Cl^-	Br^-	I^-
Li^+	0.725 –0.385	0.112 0.070	0.252 0.084	0.163
Na^+	0.284	0.145	0.131	0.120
K^+	0.203	0.129	0.117	0.093
Rb^+	0.146	0.120	0.104	0.086
Cs^+	0.114	0.098	0.078	0.062

Note. The concentration range was 0–1.2 M for the sodium and potassium salts and LiI and 0–0.5 M for rubidium and caesium salts. For LiF, the first value of K_c was measured in the range 0–0.01 M and the second in the range 0.04–0.1 M; for LiCl and LiBr, the first value of K_c was measured in the range 0–0.07 M and the second in the range 0.15–1.2 M.

It is noteworthy that two oxygen salting out coefficients can be observed in solutions of lithium salts: in the region of low (up to 0.7 M) electrolyte concentrations and in the region of high concentrations (0.15–1.2 M).[40] In the first concentration range, the coefficients K_c are greater by a factor of 2–3 than in the second. An analogous effect has been established for $NaHCO_3$.[232] The same [constant] value of K_c has been observed only for the salts LiI, Li_2SO_4, and Li_2CO_3 at concentrations in the range 0–1.2 M). Constant values of K_c have been established[13] for the salts LiCl, $LiNO_3$, and Li_2SO_4 over a wide concentration range (Table 6). The anomalous behaviour of lithium salts in relation to oxygen persists over a wide temperature range[217,220] and has been explained by the appreciable hydration of lithium ions, as a result of which the amount of free water diminishes markedly and this leads in its turn to a corresponding decrease in the solubility of oxygen.

It is seen from Tables 2–6 that there are differences in the salting out of oxygen by acids, alkalis, and salts. The replacement of hydrogen in acids by a metal cation results in an appreciable increase in K_c. The oxygen salting out coefficients K_c are smaller for many salts than for alkalis. Alkali metal, ammonium, p metal (Mg, Ca, Ba, Al) and d metal (Mn, Fe, Co, Ni, Cu, Zn) carbonates, phosphates, and borates hydrolyse, as a result of which different forms of the salts exist in solution and it is difficult to attribute the salting out coefficient to any particular form. The coefficients for the salting out of oxygen from solutions in these salts therefore require careful checking. An example is provided by the values of $K_{c\alpha}$ for the salting out of oxygen from NH_4Cl solutions obtained in two investigations.[12,218] The solubilities of oxygen in NH_4Cl solution established by MacArthur[218] have been included in many textbooks[11] and handbooks.[10] However, measurements in recent years have shown[12,13] that $K_{c\alpha}$ for oxygen in NH_4Cl solution is appreciably smaller ($K_{c\alpha}$ = 2.76 litre mol^{-1}) than the value obtained previously[218] ($K_{c\alpha}$ = 2.79 litre mol^{-1}). In order to prevent the hydrolysis of p and d metal salts, a small amount of acid (0.01–0.04 M), which does not affect appreciably the solubility of oxygen, was added by Lang and Zander.[13] One can therefore postulate that Lang and Zander[13] determined the values of $K_{c\alpha}$ for oxygen in the presence of non-hydrolysed salts.

Table 5. The coefficients K_c (litre mol^{-1}) of the salting out of oxygen from solutions of alkali metal salts with oxygen-containing anions at 298.15 K (p_{O_2} = 0.1 MPa).[40*]

Ion	ClO_4^-	NO^-	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}
Li^+	0.218 (0–0,07 M) 0.066 (0.15–1.2 M)	0.196 (0–0.07 M) –0,040 (0.15–1.2 M)	0.244 — —	0.254 — —	— — —
Na^+	0.160	0.124	0.376	0.464	0.652 (0–0.6 M)
K^+	0.150 (0–0,12 M)	0.105	0,297 (0–0,6 M)	0.379	0.507 (0–0.6 M)
Rb^+	0.138** (0–0.1 M)	0.096 (0–0,5 M)	0.290 (0–0,3 M)	—	—
Cs^+	—	0.066 (0–0,5 M)	0,255** (0–0.45 M)	—	—

*The salt concentration ranges for which the values of K_c were calculated are indicated in brackets; in the remaining cases the concentration range was 0–1.2 M.

**The values of K_c for the salting out of oxygen from $RbClO_4$ and Cs_2SO_4 solutions quoted by Battino et al.[4] are incorrect; the values from the original source[40] are quoted here.

The electron shells of s, p, and d elements have a significant influence on the values of $K_{c\alpha}$ (Fig. 2). Fig. 2 shows that $K_{c\alpha}$ for oxygen is a periodic function of the atomic number of the element in the Periodic System. The periodicity of the function is manifested by the fact that a similarity is observed between sections of the given

relation within Periods, i.e. there is a periodic variation in $K_{c\alpha}$ with increase in the atomic number of the element.

Table 6. The coefficients $K_{c\alpha}$ (litre mol^{-1}) of the salting out of oxygen from salt solutions (T = 310.2 K; p_{O_2} = 0.1 MPa).[13]

Ion	Cl^-	NO_3^-	SO_4^{2-}	HSO_4^-
Li^+	0.094 (0—3.978 M)	0.081 (0—2.869 M)	0.278 (0—1.903 M)	—
Na^+	0.131 (0—4.017 M)	0.101 (0—2.078 M)	0.334 (0—1.762 M)	0.165 (0—2.628 M)
K^+	0.124 (0—2.976 M)	0.098 (0—1.852 M)	0.331 (0—0.582 M)	0.158 (0—2.017 M)
Rb^+	0.114 (0—2.957 M)	0.095 (0—2.017 M)	0.304 (0—1.199 M)	—
Cs^+	0.099 (0—6.122 M)	0.090 (0—0.930 M)	0.295 (0—1.909 M)	—
NH_4^+	0.076 (0—3.001 M)	0.059 (0—3.120 M)	0.227 (0—3.499 M)	0.121 (0—3.010 M)
Mg^{2+}	0.202 (0—2.879 M)	0.172 (0—2.238 M)	0.280 (0—2.013 M)	—
Ca^{2+}	0.226 (0—4.477 M)	0.192 (0—1.961 M)	—	—
Ba^{2+}	0.265 (0—1.509 M)	0.223 (0—0.298 M)	—	—
Mn^{2+}	0.206 (0—2.127 M)	0.173 (0—1.936 M)	0.252 (0—1.740 M)	—
Co^{2+}	0.222 (0—1.494 M)	0.187 (0—1.487 M)	0.270 (0—1.494 M)	—
Ni^{2+}	0.214 (0—1.490 M)	0.186 (0—2.062 M)	0.271 (0—1.489 M)	—
Cu^{2+}	0.194 (0—1.517 M)	0.177 (0—1.267 M)	0.257 (0—1.000 M)	—
Zn^{2+}	0.211 (0—2.959 M)	0.181 (0—1.651 M)	0.268 (0—2.151 M)	—
Cd^{2+}	0.188 (0—2.029 M)	0.167 (0—2.046 M)	0.269 (0—3.026 M)	—
Al^{3+}	0.301 (0—2.503 M)	0.252 (0—1.095 M)	0.687 (0—0.396 M)	—
Fe^{3+}	0.219 (0—2.064 M)	0.210 (0—1.037 M)	0.438 (0—0.940 M)	—
La^{3+}	0.334 (0—2.478 M)	0.243 (0—2.227 M)	—	—
Ce^{3+}	0.347 (0—2.462 M)	0.236 (0—2.952 M)	—	—
Th^{4+}	—	0.302 (0—1.385 M)	—	—

Note. The salt concentration ranges for which the values of $K_{c\alpha}$ have been calculated are indicated in brackets; the error of the calculation of $K_{c\alpha}$ is 1—4%; the values of $K_{c\alpha}$ for the salts $ZnCl_2$ and $CdCl_2$ were calculated from the slope of the lg α—c curve in the salt concentration range 0—0.5 M.

(d) The influence of pH on the solubility of oxygen

We are aware of only two studies[236,237] in which the influence of pH on the solubility of oxygen in water and electrolyte solutions was investigated. Both in pure water and in 0.1 M CH_3COONa solution, the solubility of oxygen is independent of pH in the range from 2 to 12 at 293—313 K. Only when the pH is reduced from 2 to 0 and increased from 12 to 14 does the solubility of oxygen diminish, which is due to the presence of considerable amounts of HCl and NaOH respectively. The solubility of oxygen in 0.1 M Na_2SO_4 solution does not change when the pH is reduced from 6 to 1.

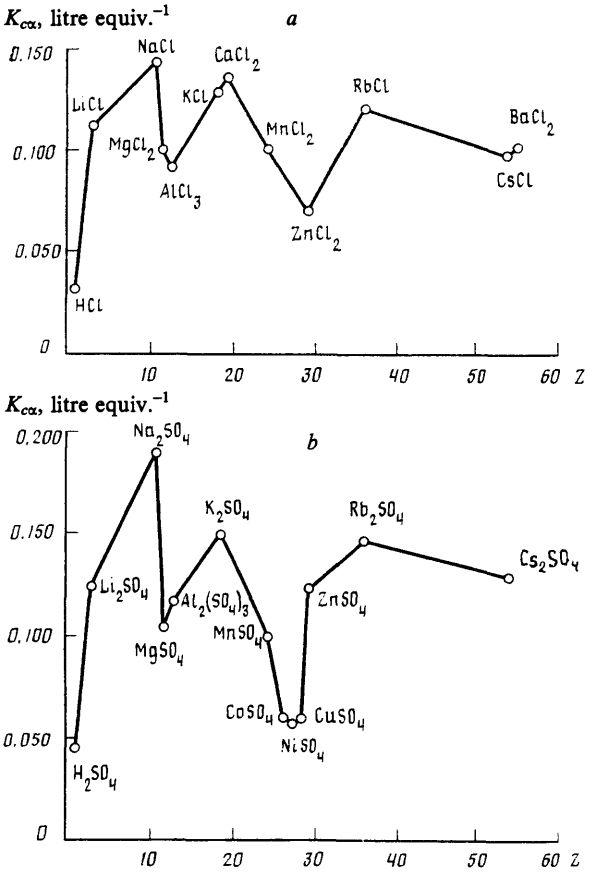


Figure 2. Dependence of the oxygen salting-out coefficient in solutions of chlorides (*a*) and sulphates (*b*) on the atomic number of the cation in the Periodic System; T = 298.15 K; p_{O_2} = 101.325 kPa (the quantities $K_{c\alpha}$ for $CoSO_4$, $NiSO_4$, and $CuSO_4$ were obtained at p_{O_2} = 5 MPa[225]).

5. The influence of temperature and pressure on the oxygen salting out coefficients

With increase in temperature, the coefficients $K_{c\alpha}$ for the salting out of oxygen from electrolyte solutions as a rule diminish.[220] The influence of temperature (in the range 298—523 K) on the values of $K_{c\alpha}$ in solutions of ammonium, copper, zinc, nickel, and cobalt sulphates and ammonium chloride is slight.[184] The temperature coefficients of the quantities $K_{c\alpha}$ depend on pressure. With increase in oxygen pressure, the coefficients for salting out from $(NH_4)_2SO_4$ solutions increase and those for salting out from NH_4OH

and $NaHCO_3$ solutions diminish.[232,238] At elevated temperatures ($T > 423$ K), the influence of pressure on the coefficients $K_{c\alpha}$ decreases. At high electrolyte concentrations (~ 0.5 M) and pressures up to 2 MPa, the coefficients $K_{c\alpha}$ diminish with increase in temperature.[232] At high temperatures ($\sim 400-428$ K) there is an inversion: with increase in temperature from 273 to 400–428 K, the coefficients $K_{c\alpha}$ diminish to a minimum and increase on subsequent increase in T (above 428 K).[202,232]

Minima in the dependence of $K_{c\alpha}$ on T are observed at temperatures exceeding by 25–50 K the temperature of the minimum solubility of oxygen in water.

6. The influence of pressure on the solubility of oxygen in electrolyte solutions

At oxygen pressures up to 3 MPa, solutions of oxygen both in water and in electrolyte solutions rigorously obey Henry's law expressed in the form applied to ideal systems.[212,229,232,239–241] The temperature and electrolyte concentration influence the behaviour of the oxygen–liquid phase systems.[201,232] At 323 K and $p_{O_2} > 3$ MPa, deviations from Henry's law are observed in dilute electrolyte solutions. With increase in electrolyte concentration, the deviations from Henry's law diminish.[232]

7. The solubility of oxygen in solutions of mixtures of electrolytes. The problem of the calculation of individual ionic oxygen salting-out coefficients

The solubility of oxygen has been investigated in solutions of mixtures of certain electrolytes.[242–248] It has been established[243–245,247] that the solubility of oxygen in solutions of mixtures of electrolytes is close to the corresponding solubility for the dominant electrolyte in the solution. However, it has been noted[248] that the salting out depends on the overall salt concentration in solution.

Solubilities of oxygen in solutions of KCl, $CaCl_2$, and $AlCl_3$ at the same equivalent concentrations and in their mixtures are the same and independent of the nature of the cation.[246] The availability of only a few and contradictory data hinders the calculation of the individual ionic oxygen salting-out coefficients and the analysis of their additivity.

We shall consider the existing literature procedures for the calculation of individual ionic oxygen salting-out coefficients. On the assumption that the salting out effect of ions and salts is additive, it has been suggested that the overall salting out effect be described with the aid of the formula:[249,250]

$$\lg (c_0/c) = \sum h_i I_i ,$$

or:[12]

$$\lg (c_0/c) = \sum K_i m_i, \qquad (12)$$

where h_i are constants referring to salts or ions, I_i are the contributions of ions of the *ith* kind to the ionic strength of the solution, K_i are individual ionic salting-out coefficients, and m_i are the molalities of the ith components (in the ionic or molecular form).

It has been suggested[251] that the salting-out coefficient be regarded as the sum of three constants characterising the behaviour of the gas (K_g), the cation (K_c) and the anion (K_a):

$$K = K_g + K_c + K_a, \qquad (13)$$

where K_g is the component of the gas salting-out coefficient independent of the nature of the electrolyte in the solution of which the gas is being dissolved and which depends solely on temperature, while K_c and K_a are the components of the salting-out coefficient referring to the cations and anions which are independent of temperature.

Van Krevelen and Hoftijzer[251] failed to give a theoretical justification of Eqn. (13) and did not indicate a method for the determination of the quantities K_g, K_c, and K_a although the values of K_c and K_a for 13 ions are quoted (Table 1). The assumption of the additivity of the salting-out coefficient underlies Eqn. (13).

The authors[251] assumed arbitrarily (without explanation) that $K_{H^+} = K_{NO_3^-} = 0$. It may be that the authors assumed that the coefficient for the salting out of oxygen from HNO_3 solutions at 298 K is lowest (Table 2). Lang and Zander[13] calculated the individual ionic oxygen salting-out coefficients on the assumption that $K_{Na^+} = 0$ (Table 7). The Na^+ ion was selected as the reference ion on the grounds that the Na_2SO_4 molecules are more effectively dissociated than H_2SO_4.

The idea of subdividing the gas salting-out coefficient into three components [see Eqn. (13)] was used by a number of workers[223,250,252] who obtained individual ionic oxygen salting-out coefficients (Table 7) from the experimental coefficients for the salting out of oxygen from electrolyte solutions by the method of least squares (i.e. by minimising the squares of the differences between the experimental K_c and the values of K_c calculated from the ionic salting-out coefficients K_i). These coefficients have been related[12] to the Sechenov constant by means of Eqn. (12), while other investigators[13,250,252] used for this purpose the equation:

$$K_{c\alpha} = 1/2 \sum_i K_i n_i Z_i^2,$$

where n_i is the number of ions of the ith kind referred to one electrolyte molecule and Z_i is the ionic charge.

For the same ions, the individual ionic salting-out coefficients, obtained by different workers, are not identical owing to the differences between the reference systems and between the methods of calculation of the ionic salting-out coefficients adopted. In order to eliminate the differences between the relative reference systems, a single reference system has been proposed.[253] It makes it possible to recalculate the ionic salting-out coefficients with the aid of the formulae

$$K_c^* = K_c - K^+, \qquad (14)$$

$$K_a^* = K_a - K^-, \qquad (15)$$

$$K_g^* = K_g + K^+ + K^-, \qquad (16)$$

and thus to compare the individual ionic oxygen salting-out coefficients obtained by different workers. In Eqns. (14)–(16), K_c and K_a, and K_g are the individual salting-out coefficients calculated by the method of least squares[223,250] or by some other procedure from the experimental values of K_c and K^+ and K^- are arbitrary constants referring to the cation and anion respectively. On adding together Eqns. (14)–(16), we obtain

$$K = K_c^* + K_a^* + K_g^*.$$

The new values of K_i^*, characterising the behaviour of the gas (K_g^*), the cation (K_c^*), and the anion (K_a^*), are evidently equivalent to the values of K_g, K_c, and K_a respectively in Eqn. (13), since the summation of the former three quantities (K_i^*) leads to the same value of K as the summation of the latter three quantities (K_i).

The NaCl solution–O_2 system, for which $K_c = K_c^*(Na^*) = 0.091$ and $K_a = K_a^*(Cl^-) = 0.021$ and which has been most thoroughly investigated, has been proposed as the reference system.[253]

Table 7. The ionic oxygen salting-out coefficients at 298.15 K.

Cation	Ionic salting-out coefficients (litre mol^{-1}) from different sources						Anion	Ionic salting-out coefficients (litre mol^{-1}) from different sources					
	[251]	[249]	[223]	[12]	[2]	[13]*		[251]	[249]	[223]	[12]	[250]	[13]*
H^+	0	0.000	−0.1110	0	−0.774	−0.200	F^-	—	—	—	—	0.982	—
Li^+	—	—	−0.0416	—	−0.664	−0.060	Cl^-	0.021	0.021	0.3416	0.029	0.844	0—257
Na^+	0.094	0.091	−0.0183	0.107	−0.550	−0.000	Br^-	0.011	0.012	0.3310	—	0.820	—
K^+	0.071	0.074	−0.0362	0.099	−0.596	−0.013	I^-	0.005	—	0.3124	—	0.821	—
Rb^+	—	—	−0.0449	—	−0.662	−0.025	OH^-	0.061	0.066	0.3875	0.081	0.941	0.340
Cs^+	—	—	−0.0584	—	−0.666	−0.041	NO_3^-	0	−0.001	0.3230	0.013	0.802	0.220
NH_4^+	0.031	0.028	−0.0737	0.033	−0.720	−0.098	ClO_4^-	—	—	—	—	0.888	—
NEt_4^+	—	—	—	—	−0.912	—	CNS^-	—	—	0.2612	—	—	—
Mg^{2+}	0.046	0.051	−0.0568	0.119	−0.314	−0.025	HSO_3^-	—	—	0.3869	—	—	—
Ca^{2+}	0.051	0.053	−0.0547	—	−0.303	−0.015	HSO_4^-	—	—	—	0.069	—	0.333
Ba^{2+}	0.060	—	−0.0473	—	−0.297	0.003	HS^-	—	—	0.3718	—	—	—
Mn^{2+}	0.046	—	−0.0625	—	−0.311	−0.029	HCO_3^-	—	—	—	0.083	—	—
Cd^{2+}	—	—	−0.0062	—	—	−0.031	SO_4^{2-}	0.021	0.022	0.3446	0.121	0.453	0.163
Zn^{2+}	0.046	0.048	−0.0590	0.108	—	−0.024	CO_3^{2-}	0.021	0.021	0.3754	—	0.485	—
Sr^{2+}	—	—	−0.0445	—	—	—	SO_3^{2-}	—	—	0.3275	—	—	—
Fe^{2+}	0.049	—	−0.0602	—	—	—	PO_4^{3-}	—	—	0.3265	—	0.320	—
Co^{2+}	0.058	—	−0.0534	—	—	−0.021							
Ni^{2+}	0.059	—	−0.0520	—	—	−0.022							
Cu^{2+}	—	—	—	—	—	−0.030							
Al^{3+}	—	—	−0.0986	—	—	−0.018							
Fe^{3+}	—	—	—	—	—	−0.032							
La^{3+}	—	—	—	—	—	−0.014							
Ce^{3+}	—	—	—	—	—	−0.015							
Th^{4+}	—	—	—	—	—	−0.017							

*At 313.15 K.

Note. The numerals in square brackets denote references (Translator).

However, a subsequent check[254] of the proposed method indicated considerable discrepancies between the ionic salting-out coefficients obtained by different workers.[12,250]

A satisfactory agreement has been established[12,223,250,252] between the experimental and calculated (assuming additivity) coefficients for the salting out of oxygen from aqueous and non-aqueous solutions of certain electrolytes. However, analysis of the oxygen salting-out coefficients based on additivity using individual ionic salting-out coefficients[12,223,250] with the aid of the constant differences law showed[254] that additivity is by no means observed in all cases. The best agreement between the experimental oxygen salting-out coefficients and the values calculated assuming additivity has been observed for nitrates, sulphates, chlorides, bromides, hydroxides, and perchlorates. Considerable discrepancies have been observed between K_{exp} and K_{calc} for fluorides, lithium salts, and lithium hydroxides, ammonium hydroxide, carbonates, and phosphates.[254] These discrepancies may be caused by the unreliability of the experimental coefficients for the salting out of oxygen from certain electrolyte solutions, the possibility of complex formation (lithium salts), and the hydrolysis of many salts (carbonates and phosphates).

V. Extrema in the influence of temperature and electrolyte concentration on the solubility of oxygen

In most modern textbooks of chemistry and physical chemistry and also in the Short Chemical Encyclopaedia and in certain monographs,[255,259] it has been reported that either all gases dissolve in liquids with evolution of heat and that the solubility of gases in liquids diminishes as the temperature is raised or that there are rare exceptions where the solubility of a gas at normal pressures increases with increase in temperature.

However, experimental facts have shown that the inversion of the influence of temperature and electrolyte concentration on the solubility of oxygen and other non-polar gases in water and electrolyte solutions is not all that rare a phenomenon. Experimental data are available concerning the presence of a minimum in the temperature variation of the solubility of oxygen not only in water[199,201,202] but also in organic and inorganic solvents,[260–262] in electrolyte solutions,[212,217,225,227] and in natural salt solutions.[202,215]

Measurements of the solubility of oxygen in pure water over a wide range of temperatures and pressures carried out most thoroughly during the last ten years have shown that the temperature of the minimum solubility of oxygen in pure water is 373 K (p_{O_2} = 0.1–5 MPa).[201,202] It is seen from Table 8 that in aqueous electrolyte solutions this temperature is lower and depends on the nature and concentration of the electrolyte (Figs. 3 and 4).[217,226,227] An increase in the electrolyte concentration shifts the region of the solubility minimum towards lower temperatures. The depth of the minimum also diminishes under these conditions. An increase in pressure from 1 to 5 MPa hardly affects the temperature of the minimum solubility of oxygen in the electrolyte solution but increases the depth of the minimum.[232]

Thus the presence of a minimum in the temperature variation of the solubility of oxygen in water and in electrolyte solutions should be regarded as a firmly established fact. The practical importance of this phenomenon is that it can be used in the development of rational conditions for the deoxygenation of sewage and industrial waters, i.e. for the deaeration process at the temperature of the minimum solubility of oxygen, for the selection of the conditions for the autoclave dissolution of sulphide products, in processes designed to protect power station equipment against oxygen, etc.[214,263]

Table 8. Experimental quantities characterising the minima in the temperature variations of the solubility of oxygen in water and aqueous electrolyte solutions.

Electrolyte	c, M	p, MPa	T_{min}, K	Refs.
H_2O		10	348	[212]
		10	348	[213]
		0.7—3.5	385	[199]
		7—14	385	[200]
		2—6	373	[214]
		1—5	373	[201]
		4.3—5.2	373	[202, 215]
KCl	0.5—2.0	10	348	[212]
NaOH	0.5—4.0	10	348	[213]
NaOH	1.0—1.5	5	373	[225]
NaOH	0.01—0.1	1—5	373	[232]
NH_4OH	2.87—8.28	5	373	[225]
KOH	0.92—16.2	0.1	373	[235]
H_2SO_4	0.5—1.5	5	373	[225]
HNO_3	8	1—6	333	[227]
HNO_3	10	1—6	323	[227]
$(NH_4)_2SO_4$	0.75—3.0	5	373	[225]
$CuSO_4$	0.5—1.5	5	373	[225]
$CoSO_4$	0.5—1.5	5	373	[225]
$NiSO_4$	0.5—1.5	5	373	[225]
$NaHCO_3$	0.1—0.5	1—5	373	[232]
$NaNO_3$	0.1—1	1—5	373	[232]
NaCl	0.85	4.3—5.2	373	[202, 215]
NaCl	2.78	4.3—5.2	353	[202, 215]
NaCl	5.09	4.3—5.2	333	[202, 215]
NaCl	1.0*	0.1	348	[217]
Na_2SO_4	1.0*	0.1	338	[217]
LiCl	1.0*	0.1	336	[217]
Li_2SO_4	0.95*	0.1	333	[217]

*Molal concentrations.

1. The salting in of oxygen by aqueous electrolyte solutions

The salting out of oxygen is characteristic of many electrolytes over a wide range of experimental conditions.[220] However, in many instances salting in takes place.[40,238,264] The salting in phenomenon has been observed for a number of electrolytes both at 298 K (LiF, $NiNO_3$,[40] HNO_3,[226,227] $Na_2B_4O_7$,[165] and tetraethylammonium bromide[264]) and at higher temperatures of ~333—423 K (LiCl, $NaBO_2$, $Na_2B_4O_7$,[220] NH_4OH,[238] HNO_3,[226,239] H_3PO_4 [231]). The salting in of oxygen in the presence of salts is observed in the range of low concentrations of the latter where most of the water is not bound to the electrolyte ions. On the other hand, for acids and alkalis salting in is observed at high electrolyte concentrations.[227,231,265] The salting in of oxygen in dilute $Na_2B_4O_7$ solutions has been explained by the formation of oxygen-borate complexes.[165]

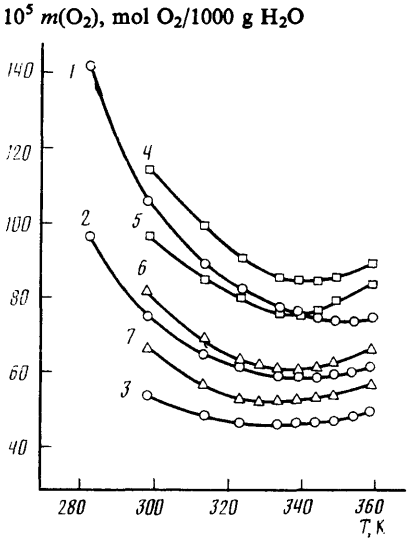


Figure 3. Temperature dependence of the solubility of oxygen in aqueous solutions of Na_2SO_4 (curves *1*—*3*), LiCl (curves *4* and *5*), and Li_2SO_4 (curves *6* and *7*) at different molalities *m*: *1* and *4*, 0.2; *2* and *6*, 0.6; *3* and *5*, 1.0; *7*, 0.95.[217]

The increase in the solubility of oxygen in HNO_3 with increase in temperature has been attributed to the decomposition of HNO_3:[266]

$$2HNO_3 \rightleftarrows N_2O_4 + H_2O + {}^1/_2O_2.$$

Apparently the inversion in the influence of the electrolyte concentration on the solubility of oxygen is associated both with the characteristics of the dissociation of electrolytes and with the formation of oxygen complexes and the structural changes occurring in solutions.

2. Theoretical justification of the inversion in the influence of temperature on the solubility of oxygen

The first explanation of the minima on the curves relating the solubilities of gases in liquids to temperature is due to Winkler.[267] On the basis of the relation between the absorption of a gas and the internal friction (viscosity) and density of the liquid, he showed that the changes in the latter two properties as a function of temperature affect the solubility of the gas in opposite ways, which leads to a minimum in the temperature variation of the solubility of the gas in the liquid.

According to Kuenen,[208] the minimum in the temperature variations of the solubilities of gases in liquids is due to the fact that, above the critical temperature of the solvent, both components mix in all proportions, i.e., as the critical point is approached, an increase in solubility should be observed. Therefore in cases where

the solubility of the gas diminishes with increase in temperature, the minimum solubility should occur at a higher temperature. Consequently the existence of a minimum is a common phenomenon and is not associated with specific properties of the solvent and the dissolved gas.

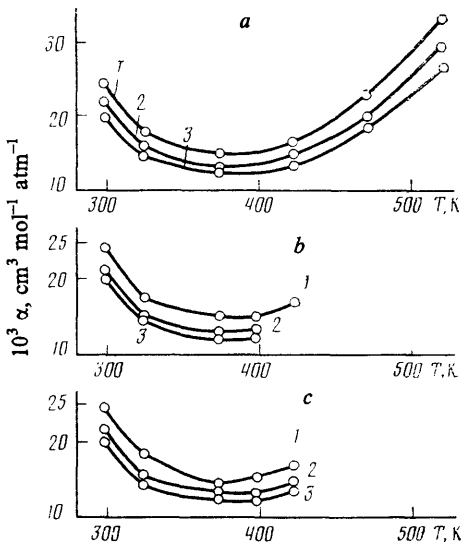


Figure 4. Temperature dependence of the solubility of oxygen in solutions of $CuSO_4$ (*a*), $CoSO_4$ (*b*), and $NiSO_4$ (*c*) at different salt concentrations (M): *1*, 0.5; *2*, 1.0; *3*, 1.5.[225]

The next attempt to explain the presence of a minimum in the curves for the temperature variation of the solubilities of gases in water was made by Tammann[211] in 1926 on the basis of the hydration theory. However, the gas solubility minima are encountered also in non-aqueous solvents.[260–262]

According to modern ideas,[268,269] there are two mechanisms of the dissolution of a gas in water and in aqueous electrolyte solutions: the filling of vacancies and the substitution of water molecules in the structural framework of water. These two mechanisms have been called vacancy and solvation mechanisms by Borina and Samoilov,[268] the insertion and insertion-substitution mechanisms by Frank and Quist,[270] and the hydrophobic and hydrophilic mechanisms by Krestov.[271] The diminution of the vacancy contribution and the increase in that of the solvation contribution with increase in temperature are responsible for the presence of a minimum in the curves for the temperature variation of the solubility of oxygen (as well as other non-polar gases in water).[268]

The phenomenon of inversion in the influence of temperature on the solubility and the salting-out coefficients of oxygen in water and in electrolyte solutions can be understood in the light of the thermodynamic theory[272–274] and with the aid of the structural model of solutions of non-polar gases in water.[272,275] The presence of a minimum in the curves for the temperature variation of the solubility of oxygen implies that the dissolution is exothermic at $T < T_{min}$ and endothermic at $T > T_{min}$. On the assumption that the ice-like framework is stabilised in the vicinity of the gas molecule, the minimum in the temperature variation of the solubility of a gas has been explained[272] with the aid of thermodynamic analysis. The partial molar enthalpy of solution of the gas was expressed in the form

$$\bar{H}_2 = \bar{H}_2^0 + \Delta\bar{H}^0\left(\frac{\partial\nu}{\partial y}\right)_p - \overline{H}_2^\circ + H_2^{st},$$

where $\overline{H}_2^\circ$ is the partial enthalpy of gas molecules in solution subject to the exclusion of the structural contribution corresponding to the redistribution of the molecules between the vacancies and the framework, $\Delta\overline{H}^\circ$ is the enthalpy of the transfer of one mole of water from the cavities in the water structure to the framework, ν is the fraction of water molecules at the lattice sites of the framework, and $y = N_2/N_1$, N_1 and N_2 being the numbers of water and gas molecules in the system. The structural component H_2^{st} diminishes with increase in temperature, because $\Delta\overline{H}^\circ$, defined by the formula

$$\left(\frac{\partial\nu}{\partial y}\right)_p = \nu(1-\nu)[\nu - 2(1-\nu)] \cdot \frac{\Delta\bar{H}^0}{RT^2},$$

decreases with increase in temperature. The structural component of the hydrophobic hydration of a gas diminishes with increase in temperature, while the exothermic component of the transfer of molecules from the vacancies in the water structure to the framework disappears, as a result of which the overall heat of solution of gases becomes positive.

A method has been proposed[276] for the determination of the temperature of the minimum solubility of a gas in a liquid. For this purpose, the relation between the standard thermodynamic characteristics calculated from the solubility (ΔH_2°) and in terms of the phase distribution constant ($\Delta H_2^\ominus$) is expressed in the form

$$\Delta H_2^\ominus = \Delta H_2^\circ - \Delta H_{cond,1}^\circ, \qquad (17)$$

where $\Delta H_{cond,1}^\circ$ is the standard enthalpy of condensation of the solvent under a pressure p_1.

In contrast to the generally adopted approach in the study of the dissolution of a gas in a liquid (G⇄S), Krestov and Kudryavtsev[276] suggested that account be taken of the composition of the vapour phase, i.e., that the dissolution should be described by G + V⇄S, where G, V, and S are respectively the symbols for the gas, the vapour, and the solvent in the solution.

Since at the temperature of the minimum solubility of the gas $\Delta H_2^\circ = 0$, Eqn. (17) becomes:

$$\Delta H_2^\ominus = -\Delta H_{cond,1}^\circ,$$

The point of intersection of the $\Delta H_2^\ominus(T)$ and $\Delta H_{cond,1}^\circ(T)$ relations defines the temperature of the minimum solubility of the gas.

The experimental data show that the temperature dependence of the oxygen salting-out coefficient is also described by a curve with a minimum.[215,232] In the literature attempts have been made[274] to establish the causes of the inversion in the influence of temperature on the coefficients for the salting-out of non-polar gases from aqueous electrolyte solutions.

The temperature dependence of the coefficient of the salting out of a gas from aqueous solutions has been found:

$$\left(\frac{\partial K_{c\alpha}}{\partial T}\right)_p = \frac{H_1 - H_1^*}{2{,}3\,mRT^2} = \frac{\partial \lg (f_1^*/f_1^0)}{\partial T}, \qquad (18)$$

where H_1 and H_1^* are the enthalpies of water molecules in water and in solution, f_1^* and f_1° are the fugacities of water over the solution and pure water, and m is the molal electrolyte concentration. The

experimental vapour pressures of water over electrolyte solutions show that the differences $H_1 - H_1^* > 0$ and increase with temperature. In conformity with Eqn. (18), the quantities $K_{c\alpha}$ should increase more rapidly with temperature at high values of the latter.[274] However, it is not stated[274] why $K_{c\alpha}$ decreases with increase in temperature at low values of the latter.

On combining the Gibbs–Helmholtz equation and the Sechenov equation, one can obtain

$$\frac{\partial K_{c\alpha}}{\partial T} = \frac{(H_2)_{H_2O} - (H_2)_{soln}}{2.3\, mRT^2} = \frac{1000}{m\rho} \frac{\partial \lg (f_2/f_2^0)}{\partial T} - K_{c\alpha} \frac{\partial \ln \rho}{\partial T},$$

where $(H_2)_{H_2O}$ and $(H_2)_{soln}$ are the enthalpies of dissolved oxygen molecules in pure water and in solution respectively, ρ is the density of the solution, and f_2^0 and f_2 are the fugacities of dissolved oxygen in pure water and in solution.

Apparenty both the appearance of a minimum on the curves relating the solubility of oxygen to temperature and the minimum in the temperature dependence of $K_{c\alpha}$ are caused by the structural changes in the solution, i.e. the quasi-clathrate (vacancy) and quasi-crystalline (solvation) structures of the oxygen solution predominate at low and high temperatures respectively. The temperature-dependent differences in the nature of the oxygen dissolution process are caused by the different relative enthalpies of dissolved oxygen in water and in the solution, which leads to a minimum on the curves for the temperature variation of the salting-out coefficient.

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The great role of oxygen in many chemical, biochemical, electrochemical, ecological, and corrosion processes has made it necessary to know its solubility in water and in electrolyte solutions. This requires in turn the existence of precise, highly sensitive and convenient methods for the determination of the concentration of dissolved oxygen. Electrochemical methods, in particular membrane voltammetric sensors, which make it possible to measure the concentration of dissolved oxygen in various gas–liquid systems over a wide range of experimental conditions, have come to be most widely used during the last five years. However, the smallest error (less than 0.1%) can be achieved with the aid of the volumetric method.

Despite the large number of methods of expressing the solubility of oxygen, preference has been given at the present time to the Henry coefficient (K_H) and the mole fraction (X_2).

The solubility of oxygen in water is the recommended standard quantity in the measurements of the solubilities of gases in liquids.

Temperature and the nature and concentration of the electrolytes exert a significant influence on the solubility of oxygen in water. The problem of the individual ionic oxygen salting-out coefficients has been discussed for the first time.

The greatest advances have been made in the study of the influence of temperature and the nature and concentration of electrolytes on the solubility of oxygen. Such studies have led to the discovery of extrema involving a change in the sign of the temperature variation of the solubility of oxygen in water and in electrolyte solutions and also a change from salting out to salting in (or conversely) with increase in the concentrations of certain electrolytes and temperature.

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Interaction of uranium oxides with dinitrogen tetroxide

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ABSTRACT. Data on the interaction of nitrogen oxides in different oxidation states with dinitrogen tetroxide in the temperature range 273–1073 K and in the pressure range 0.1–10 MPa are surveyed. The mechanisms of the interaction of the dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system, liquid N_2O_4, and N_2O_4–organic solvent mixtures with uranium oxides are discussed as a function of the oxidation state of uranium, the specific surface and structure of the oxides, the state of aggregation of N_2O_4, the presence of impurities in the latter, and the presence of organic solvents. The behaviour of uranium oxides in relation to that of the other metal oxides is subjected to a comparative analysis.

The bibliography includes 91 references.

Contents

I. Introduction 728
II. Interaction of uranium oxides with liquid dinitrogen tetroxide 729
III. Interaction of uranium oxides with the gaseous dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system 732
IV. Interaction of uranium oxides with N_2O_4–organic solvent mixtures 735

I. Introduction

The present development of chemical industry and engineering requires the use of non-traditional liquid media (non-aqueous and mixed solvents) with a wide range of varied properties. They make it possible to solve problems involving the optimisation of processes, ecological problems, the creation of waste-free technologies, etc., which are in principle impossible in aqueous solutions.

In the field concerned with the use of non-aqueous solvents, there has been in recent years the most vigorous accumulation of qualitative and quantitative data necessary for the study of the general characteristics of the behaviour of such media and for the creation of theoretical foundations for processes involving interactions in non-aqueous solvents.

Liquid dinitrogen tetroxide N_2O_4 is a typical representative of the class of non-aqueous inorganic solvents. Its physicochemical properties had been investigated previously for the purposes of preparative chemistry in the synthesis of anhydrous nitrates. A new stage in the study of the properties of N_2O_4 involved its application as an oxidant in rocket engines and later as a possible heat exchanger in atomic power stations.[1–4]

N_2O_4 is known to be a very reactive chemical substance which can exist in both liquid and gaseous states depending on the conditions. The chemical properties of N_2O_4 in different states of aggregation differ appreciably. At atmospheric pressure, N_2O_4 exists in the liquid state at temperatures in the range 261.8–294.15 K. The temperature range of the stability of liquid N_2O_4 extends to 473, 523, and 553 K and pressures of 0.5, 2.0, and 10 MPa respectively.

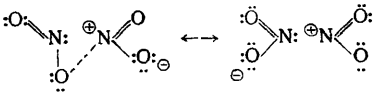
In the temperature range 263–283 K, N_2O_4 has a high density (1.470–1.515 g cm^{-3}), a low viscosity (0.468–0.599 cP),[4] and a low surface tension, amounting to 26.5 dyn cm^{-1} at 293 K and comparable to that of many volatile organic solvents. The electrical conductivity of N_2O_4 (10^{-12} Ω^{-1} cm^{-1}) is much lower than the corresponding values for liquid NH_3 and H_2O (10^{-11} at 239.6 K and 10^{-8} and 293 K).[5] The dielectric constant of liquid N_2O_4 is only 2.42 at 291 K [6] and its dipole moment is close to zero.[6]

The structures of the gaseous and solid tetroxide have been discussed in a number of studies.[7–9] According to revised data,[9] the r(N–N) distance in gaseous N_2O_4 is 0.1782 ± 0.0008 nm, r(NO) = 0.1190 ± 0.0001 nm, and ∠ONO = 135.4°. In the solid state, r(N–N) is reduced to 0.174 nm and the angle is reduced to 126°.[8] The structure of N_2O_4 has a number of features. While the N_2O_4 molecule is planar, its N–N bond length is unusually large (greater by 0.03 nm than in N_2H_4 and N_2F_2). The interatomic distances in the NO_2 groups are virtually the same as in the NO_2 molecule. The latter is consistent with the low dissociation constants of N_2O_4 at 293 K (3.43×10^{-4}–2.6×10^{-3}). It has been suggested,[10] within the framework of the valence bond method, that the greatest energy contribution to the stabilisation of the planar structure comes from the structure involving three-electron O···O bonds between the *cis*- and *trans*-oxygen atoms as a consequence of the resonance

$$O\cdot{:}O^- \leftrightarrow O\cdots O \leftrightarrow O^+{:}\,O^- \leftrightarrow O^-{:}\cdot\,O^+,$$

and

$$O^-{:}\cdot O \leftrightarrow O\cdot{:}O \leftrightarrow O^-{:}\cdot O^+.$$



Of the 21 types of ionic and covalent structures described in a N_2O_4 molecule, only one has the N–N bond, which explains, according to the author,[10] the greater bond length than the value corresponding to a single bond. The oxide N_2O_4 is capable of self-ionisation and dissociation in accordance with the schemes

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-,$$
$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-. \qquad (2)$$

The ion pairs $[NO_2^+][NO_2^-]$ and $[NO^+][NO_3^-]$ are formed in the first stages of these processes. Since the formation of nitrites was not observed on treating metals and their salts with liquid N_2O_4,[4] it has been suggested that oxygen exchange takes place immediately after

dissociation in accordance with Scheme (3):

$$NO_2^+ + NO_2^- \rightleftharpoons NO^+ + NO_3^-. \quad (3)$$

It has been established[4,11,12] that liquid N_2O_4 interacts with alkali and many other metals (Ag, Zn, Cu, Hg). Pure N_2O_4 does not interact with the majority of metals. In order to achieve reaction, use is made of mixtures of N_2O_4 with organic solvents which are capable of increasing the dielectric constant and the degree of dissociation of N_2O_4 according to Schemes (1) and (2). In the reactions with metals, an electron is transferred from the metal atom to the NO^+ ion:

$$M + N_2O_4 \rightarrow MNO_3 + NO. \quad (4)$$

The products of the reactions of N_2O_4 with metals are nitrates as well as adducts of nitrates with N_2O_4.

At atmospheric pressure, N_2O_4 exists in the liquid state up to 294 K. The brown colour of the liquid is due to the presence of nitrogen dioxide formed via the reaction $N_2O_4 \rightleftarrows 2NO_2$. With increase in temperature, the liquid is converted into a gas with the subsequent dissociation $2NO_2 \rightleftarrows 2NO + O_2$. A characteristic feature of $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system is that individual components do not exist in a pure form,[1-3] always forming an equilibrium mixture. The system behaves as an integral whole and is characterised by its physical and thermophysical properties which have been analysed in detail.[1-3]

The forward and reverse $N_2O_4 \rightleftarrows 2NO_2$ reactions take place at very high rates even at room temperature and the equilibrium between N_2O_4 and NO_2 is established almost instantaneously. N_2O_4 dissociates via the formation of an excited $N_2O_4^*$ molecule; ΔH for the reaction $N_2O_4 \rightleftarrows 2NO_2$ at 298.16 K is 57.11 kJ mol^{-1}.[13] With increase in temperature, the rate of dissociation of N_2O_4 rises and at 430–450 K the reaction equilibrium is almost wholly displaced to the right. At higher temperatures, the reaction $2NO_2 \rightleftarrows 2NO + O_2$ takes place and its equilibrium is established in 10^{-3}–10 s depending on the temperature and pressure. With increase in pressure, the equilibrium is displaced to the left in both reactions.

Oxides of the type NO_3, N_3O_6, and N_2O_2 and the radicals NO_3^- are formed as intermediates in the system. Apart from reversible processes, there is also a possibility of irreversible processes with formation of N_2O_3, O_3, N_2, N_2O, and O_2.

II. Interaction of uranium oxides with liquid dinitrogen tetroxide

We shall consider below the interaction of uranium oxides with liquid and gaseous dinitrogen tetroxide over a wide range of temperatures and pressures, because these processes have been studied most fully.

It follows from Addison's studies that metallic uranium interacts with liquid N_2O_4 only after the addition of nitrosyl chloride[14] and alkylammonium nitrates[15] or organic solvents (ethyl acetate, methyl acetate, nitromethane, etc.[16]). The processes are completed by the formation of $UO_2(NO_3)_2.N_2O_4$, $RHN_3[UO_2.(NO_3)_3]$, or $UO_2(NO_3).mL$, where L is an organic base. It follows from a number of investigations[15,17,18] that uranium oxides either do not interact at all with liquid N_2O_4 or react with it extremely slowly.

In characterising the chemical behaviour of uranium oxides, one should note that, among metal–oxygen systems, one of the most complex is the uranium–oxygen system because of the ability of uranium to form compounds in different oxidation states and also because of the existence of oxides in several polymorphic modifications and the formation of non-stoichiometric compounds. Makarov[19] put forward the hypothesis that uranium oxides obey the general homologous U_yO_{2y+2} relation; a vanishingly small change in the chemical composition of the oxides takes place in this series with increase in y and the composition tends to UO_2. Data on uranium oxides have been surveyed by Vlasov et al.[20]

UO_3 has the largest number of polymorphic forms, the existence of seven crystalline α-, β-, γ-, δ-, ε-, ξ-, and η-forms and one amorphous form of UO_3 being known.[21-25] There is a correlation between the specific surfaces of the trioxides and their reactivities in relation to oxygen.[20,26] The following crystalline modifications of U_3O_8 have been reported in the literature: α-, α′-, β-, and γ-U_3O_8.[27-29]

$(UO_3)_{am}$ has been obtained[30,31] by heating up $UO_4.2H_2O$ at temperatures in the range 623–723 K, ε- and γ-UO_3 have been prepared by the method described by Hoekstra and Siegel,[27] and "active" UO_2 has been obtained by decomposing $UO_2C_2O_4.3H_2O$.[30] The oxides UO_2, $(UO_2)_{act}$, U_3O_8, $(UO_3)_{am}$, β-UO_3, ε-UO_3, and γ-UO_3 had the following specific surfaces (m^2 g^{-1}): 2.7, 89.0, 1.5, 9.7, 7.4, 2.8, and 0.9 respectively. Uranium oxides were brought into contact with liquid N_2O_4 in sealed tubes with stirring.[31]

When $(UO_3)_{am}$ is introduced into liquid dinitrogen tetroxide, the latter boils vigorously and the liquid acquires a blue-green colour, indicating the formation of N_2O_3. The rate of interaction of $(UO_3)_{am}$ with liquid N_2O_4 depends on the initial treatment in the synthesis of the oxide $(UO_3)_{am}$ and in the first place on the conditions under which $UO_4.2H_2O$ was heated. The presence of traces of water in the oxide has a catalytic effect on the process.

The results of chemical analysis are consistent with the presence in the final product of components having the overall compositions $UO_2(NO_3)_2.2NO_2$ and $UO_2(NO_3)_2.N_2O_4$. It has been suggested[32] that the formula of the compound be written as $NO[UO_2(NO_3)_3]$. The identification of the complex as an adduct of uranyl nitrate with dinitrogen tetroxide[15] was based on the presence in its IR spectrum of low-intensity bands in the range 1730–1770 cm^{-1} corresponding to absorption by N_2O_4.[31-34] Such an identification is not unambiguous, because bands in the range 1700–1800 cm^{-1}, corresponding to the compound absorption frequencies of NO_3^- are also manifested in the IR spectra of different nitrates.[35,36]

In order to infer the structure of the compound, its vibrational spectra were compared[37] with the spectra of potassium, rubidium, caesium, and ammonium trinitratouranylates,[38,39] which were virtually identical as regards the intensity and location of the absorption bands of the nitrate groups and the uranyl ion (Table 1).

The vibrations of the nitrate groups correspond to the symmetry point group C_{2v}, which has six bands active in the IR spectra ($3A_1 + B_1 + 2B_2$). According to the ideas of Katzin[40] and Field and Hardy,[41] the splitting of the ν_4–ν_1 bands, amounting to 270 cm^{-1}, corresponds to the bidentate binding of the nitrate groups in the compound. Its IR and Raman spectra contain a narrow moderately intense band at 2294 cm^{-1}, which is absent from the spectra of complexes incorporating alkali metals. It is characteristic of the vibrations of the nitrosonium ion.[42,43] Consequently the product of the interaction of $(UO_3)_{am}$ with liquid N_2O_4 has the same structure as rubidium, caesium, potassium, and ammonium trinitratouranylates. It undergoes purely electronic transitions in the luminescence spectra close to those of the uranylates {21 235 and 21 203 cm^{-1} for $NO[UO_2(NO_3)_3]$ and $Rb[UO_2(NO_3)_3]$ [37]}.

In conformity with the formula $NO[UO_2(NO_3)_3]$, nitrogen was detected in the complex in the +3 and +5 oxidation states. It was determined by a standard method.[44]

Table 1. Vibrational frequencies of nitrosonium trinitratouranylate.[37]

IR	Raman	Assignment	IR	Raman	Assignment
2294	2295	ν (NO^+)	748	750	ν_3 (O_2NO^-)
1525	1522	ν_4 (O_2NO^-)	734	743	
1255	—	ν_1 (O_2NO^-)	710	714	ν_5 (O_2NO^-)
1025	1028	ν_2 (O_2NO^-)	690	—	
940	—	ν_3 (UO_2^{2+})	260	—	ν_2 (UO_2^{2+})
			250	234	
875	871	ν_1 (UO_2^{2+})	225	—	ν (U—O_3NO)
801	—	ν_6 (O_2NO^-)	210	182	δ (U—O—U)
			—	165	

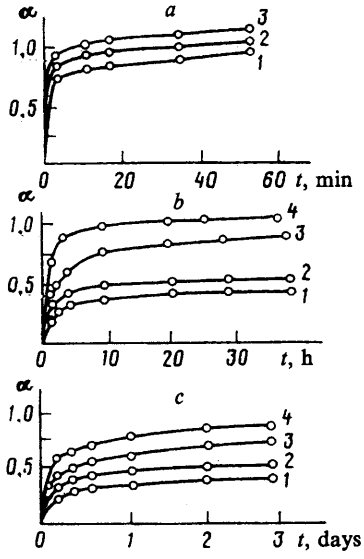


Figure 1. Dependence of the degree of conversion α of uranium trioxides $(UO_3)_{am}$ (*a*), ε-UO_3 (*b*), and γ-UO_3 (*c*) in liquid dinitrogen tetroxide on time (*t*) at different temperatures (K): *1*, 293; *2*, 323; *3*, 373; *4*, 423.

The formation of nitrosonium trinitratouranylate (NTN) on interaction of amorphous uranium trioxide with liquid N_2O_4 indicates the dissociation of the latter in accordance with Scheme (2). The reaction can be represented by the equation

$$UO_3+3N_2O_4=NO[UO_2(NO_3)_3]+N_2O_3\,. \qquad (5)$$

The product of the reactions of β-UO_3, ε-UO_3, and γ-UO_3 with liquid N_2O_4 is also NTN, but the above oxides react at a lower rate than $(UO_3)_{am}$. The properties of the oxide ε-UO_3 are closest to those of $(UO_3)_{am}$. Its degree of conversion into NTN in 1 h was 0.8 and that of ε-UO_3 was 0.25. NTN is formed from ε-UO_3 only after a month and its formation from γ-UO_3 requires more than half a year. With increase in temperature, the degrees of conversion of all the modifications of uranium trioxide in liquid N_2O_4 increase.[45] Fig. 1 illustrates the time variation of the degree of reaction of the oxides UO_3 with N_2O_4 in the temperature range 293–423 K. It is seen that the rate of reaction is especially high in the initial instant (10–30 min), after which the process gradually slows down and the time variation of α becomes almost linear. It has been observed by X-ray diffraction that the interaction is not accompanied by the formation of any intermediates.

Heterogeneous processes have been described satisfactorily by the equation $\alpha = 1 - \exp(-kt^n)$,[46] where *t* is the time and *k* and *n* are constants. (The quantity *n* indicates the region where heterogeneous reactions take place.)

Least squares treatment of the experimental data in terms of the variables $y = \lg[-\lg(1-\alpha)]$ and $x = \lg t$ yielded a slope *n* of the straight line less than 0.5 for all the modifications of uranium oxides (Table 2),[45] which corresponds to the diffusion of N_2O_4 to the surfaces of the initial uranium trioxides.

Table 2. The values of *n* and $\lg K$ for the reactions of uranium trioxides with liquid N_2O_4.

T, K	$(UO_3)_{am}$		ε-UO_3		γ-UO_3 $(UO_3)_{am}$	
	n	$\lg K$	*n*	$\lg K$	*n*	$\lg K$
293	0.46	−0.91	0.23	−5.07	0.20	−6.90
323	0.44	−0.54	0.28	−4.35	0.16	−6.23
348	0.48	−0.35	—	—	0.24	−5.13
373	0.39	−0.11	0.38	−2.73	0.19	−4.73
398	—	—	—	—	0.32	−3.80
423	—	—	0.45	−1.92	0.12	−3.68

The reaction rate constants calculated from the equation $K = nk^{1/n}$ [47] are greater by almost 5–7 orders of magnitude for $(UO_3)_{am}$ than for ε- and γ-UO_3 (Table 2).

The slopes of the $\lg K - 1/T$ relation where 0.57 ± 0.13, 3.01 ± 0.15, and 3.30 ± 0.22 for $(UO_3)_{am}$ and ε- and γ-UO_3 respectively. The empirical equations for the temperature variations of the rate constants for the reactions of the oxides with liquid N_2O_4 are as follows:[45]

$$(UO_3)_{\text{ам}}: K=10^{4.36\pm0.43}\cdot\exp-(10\,800\pm2500)/RT,$$
$$\varepsilon\text{-}UO_3: K=10^{5.20\pm0.46}\cdot\exp-(53\,300\pm2900)/RT,$$
$$\gamma\text{-}UO_3: K=10^{4.22\pm0.63}\cdot\exp-(63\,000\pm4200)/RT.$$

The lowest apparent activation energy E_A for the reaction with liquid N_2O_4 corresponded to the amorphous uranium trioxide (10.8 kJ mol^{-1}) and proved to be appreciably smaller than the energy of the dissociation of the N—N bond via the reaction $N_2O_4 \rightleftarrows 2NO_2$ (ΔH = 53.86 kJ mol^{-1} [11]). A linear relation is

observed between E_A for the formation of NTN from different uranium oxides and the specific surfaces of the latter[45] (Fig. 2). The differences between the reaction rate constants and the apparent activation energies for the reactions of the polymorphic forms of uranium trioxide with liquid N_2O_4 are probably caused by the structural features of the oxides. On passing from amorphous uranium trioxide to the crystalline modifications (β-UO_3, γ-UO_3, ε-UO_3), the quantity E_A increases by ~41.8 kJ mol^{-1}. The product of the reactions of U_3O_8 and UO_2 in the temperature range 293–423 K is also NTN. The curves for the time variation of the degrees of conversion of uranium oxides indicates the acceleration of the process with increase in temperature (Fig. 3).[45] The oxide U_3O_8 is more reactive than γ-UO_3. The conversion of U_3O_8 into NTN at 293, 323, 373, and 423 K takes place after ~180, 35, 5, and 1 days, while the corresponding times for UO_2 are 240, 100, 80, and 5 days. The rate of the process is limited by the diffusion of liquid dinitrogen tetroxide to the surface of uranium oxide. After 10–30 min, the rate of reaction falls owing to the formation of a layer of the reaction product on the surface of the oxide (n < 0.5) (Table 3).

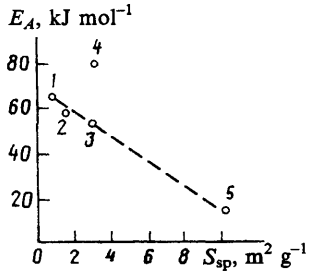


Figure 2. Dependence of the apparent activation energy E_A for the reaction of uranium oxides with liquid dinitrogen tetroxide on the specific surface of the oxide S_{sp}: *1*, γ-UO_3; *2*, U_3O_8; *3*, ε-UO_3; *4*, UO_2; *5*, $(UO)_{3am}$.

In discussing the mechanism of the interaction of uranium oxides with liquid N_2O_4, it is of interest to compare the apparent activation energies obtained from oxides having approximately the same specific surfaces but different oxidation states of uranium: ε-UO_3, U_3O_8, and UO_2 (S_{sp} = 2.8, 1.5, and 2.7 m^2 g^{-1}). On passing from the trioxide to U_3O_8 and UO_2, E_A increases and amounts to 53.3, 56.9, 75.7 kJ mol^{-1}. These data suggest that the conversion into NTN is preceded by the uranium oxidation stage. The approximate energy expenditures on the oxidation of U_3O_8 and UO_2 to the hexavalent state in liquid N_2O_4 were about 4 and 20 kJ mol^{-1} respectively. As a consequence of the oxidation of UO_2, the activation energy E_A for its interaction with N_2O_4 does not fit on the linear dependence of E_A on the specific surface of the oxide (Fig. 2).

The reactivities of the uranium oxides are probably determined not only by the state of their surfaces but also by the oxidation state of uranium in the oxide. This can be seen also in relation to amorphous UO_3 and $(UO_2)_{act}$. Although the apparent activation energy for the interaction of the oxides with N_2O_4 diminishes with increase in their specific surface, E_A for the "active" UO_2 amounted to 43.4 ± 1.88 kJ mol^{-1} compared with 10.9 kJ mol^{-1} for $(UO_3)_{am}$ despite the fact that S_{sp} for $(UO_2)_{act}$ ≃ 89.0 m^2 g^{-1} [30] is almost an order of magnitude higher than for $(UO_3)_{am}$. The value of E_A for the oxidation of "active" UO_2 to the trioxide is correlated with the values obtained for the crystalline specimens.

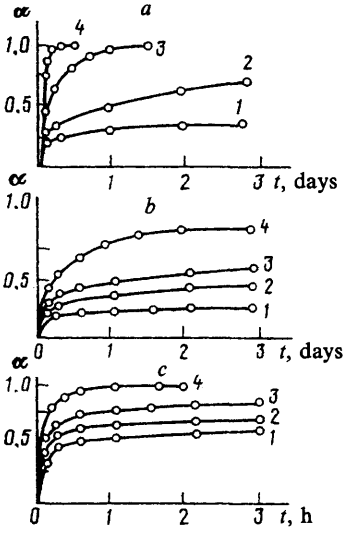


Figure 3. Time variation of the degree of conversion of the uranium oxides U_3O_8 (*a*), UO_2 (*b*), and $(UO_2)_{act}$ (*c*) in liquid dinitrogen tetroxide at different temperatures (K): *1*, 293; *2*, 323; *3*, 373; *4*, 423.

Table 3. The values of n and lg K for the reactions of the oxides U_3O_8 and UO_2 with liquid dinitrogen tetroxide and the mixture of N_2O_4 with 15% of $N_2O_3^*$ in the temperature range 293–423 K.[45]

T, K	U_3O_8				UO_2				$(UO_2)_{act}$	
	n	$-\lg K$	n^*	$-\lg K^*$	n	$-\lg K$	n^*	$-\lg K^*$	n	$-\lg K$
293	0.26	4.74	0.26	5.25	0.20	5.70	0.26	5.14	0.14	3.12
323	0.35	3.73	0.35	4.06	0.17	6.01	0.22	4.98	0.23	2.14
343	0.41	3.41	0.41	3.41	0.21	5.20	0.18	5.30	0.30	1.89
373	0.51	2.61	0.48	2.67	0.29	4.43	0.29	4.80	0.24	1.64
398	0.54	2.31	0.59	2.30	0.25	4.13	0.24	4.10	0.28	0.97
423	0.46	1.78	0.49	1.76	0.35	3.18	0.29	3.35	0.35	0.75

The conversion of "active" UO_2 into NTN is completed after 48, 36, 24, and 2 h at 293, 323, 373, and 423 K respectively. The interaction of U_3O_8 and UO_2 with liquid N_2O_4 can be represented by the following schemes:

$$U_3O_8+10N_2O_4=3NO[UO_2(NO_3)_3]+4N_2O_3, \quad (6)$$

$$UO_2+4N_2O_4=NO[UO_2(NO_3)_3]+2N_2O_3. \quad (7)$$

Since dinitrogen tetroxide contains as a rule admixtures of N_2O_3, the influence of the addition of this component on the reactions was investigated. It is also seen from Eqns. (6) and (7) that N_2O_3 is a reaction product and may accumulate in the reaction mixture. In experiments with different N_2O_3 contents, it was noted that in the temperature range 293–423 K the product of the reactions of all the uranium oxides is NTN. It follows from the data in Table 3 that the introduction of 15% of N_2O_3 does not influence significantly the process kinetics in the temperature range 323–423 K. Some differences are observed at temperatures below 323 K; here the rate of reaction in the $N_2O_4-N_2O_3$ mixtures is higher than in N_2O_4 (Table 3).[48] A similar behaviour has been shown also by metallic zinc.[49] The apparent activation energies for the interaction of UO_2 and U_3O_8 with $N_2O_4-N_2O_3$ mixtures were found to be 76.48 ± 17.6 and 52.8 ± 1.63 kJ mol^{-1} respectively.[45] They are close to the values obtained for pure N_2O_4.

The increase in the rates of reaction of uranium oxides with liquid N_2O_4 in the presence of admixtures of N_2O_3 is caused by the increase in the concentrations of the NO^+ and NO_3^- ions, since N_2O_3 shows a greater tendency towards dissociation than N_2O_4. As a consequence of the dissociation of N_2O_3, according to the schemes

$$2N_2O_3 \rightleftharpoons 2NO+2NO_2 \rightleftharpoons [NO^+][NO_3^-]+2NO, \quad (8)$$

$$N_2O_3 \rightleftharpoons NO+NO_2, \quad (9)$$

$$2NO_2 \rightleftharpoons NO^+ + NO_3^-, \quad (10)$$

the amount of the reactive ion pairs $[NO^+][NO_3^-]$ as well as NO^+ and NO_3^- ions in solution increases. With increase in temperature, the degree of dissociation of N_2O_4 itself also rises appreciably and abolishes the effect of the dissociation of the added N_2O_3 observed at lower temperatures. Presumably the addition of more than 15% of N_2O_3 would also increase the kinetic parameters of the processes investigated at temperatures above 323 K, as was observed by Addison et al.[49]

Since the processes under discussion are extremely difficult to carry out in the absence of traces of water, a study has been made[31] of the influence of added H_2O on the kinetics and the composition of the reaction products. It was noted that the introduction of water appreciably increases the degree of conversion of the oxides. Thus the reaction of amorphous UO_3 in the presence of 0.2% of water is completed after 15 min and with increase in the water content the rate of reaction increases still further. The acceleration of the process has been observed also for other modifications of UO_3 as well as U_3O_8. The degree of conversion of ε-UO_3 in the presence of a water content of about 3% is 65% (45% for anhydrous ε-UO_3) and the reaction reaches completion after 20 days.

Uranium dioxide behaves somewhat differently.[31] When the water content on the surface of the oxide is less than 1.5%, its reactivity hardly changes, whereas in the presence of larger amounts of water the process is appreciably accelerated and in the presence of 15% of water it takes place almost instantaneously. The acceleration of the process in the presence of water is probably induced by the formation of nitric acid, which activates the surface and increases the content of NO_3^- ions.

III. Interaction of uranium oxides with the gaseous dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system

The interaction of uranium oxides with the dissociating system has been investigated under dynamic and static conditions at 293–1073 K.[50–52] In the experiments under dynamic conditions, powders of the uranium oxides were placed in a tubular furnace heated to a specified temperature. The stability of the pressure in the gas stream was achieved by maintaining liquid N_2O_4 at the boiling point (294 K) in a thermostatted cell. The contact time was 5 h in all the experiments. The interaction of uranium oxides with the gaseous dissociating system at 323–873 K and at pressures in the range 0.5–10 MPa was carried out in thick-walled glass tubes, the lower part of which was filled with liquid N_2O_4 (it was frozen with liquid nitrogen before the experiment), while uranium oxides were placed in the upper part of the tube on a special suspension. The tube was sealed off and electric furnaces were moved over its lower and upper parts. The furnace over the lower part of the tube served to ensure a constant N_2O_4 pressure during the experiment, while the necessary reaction temperature was maintained with the aid of the furnace over the upper part of the tube. (The pressure developed in the tube was calculated from the temperature dependence of the $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ vapour pressure over the liquid, as described by Nesterenko et al.[1]) At the end of the experiment, the tube was removed from the furnaces, cooled rapidly with liquid nitrogen, and then opened.

Amorphous UO_3 readily reacts in the $N_2O_4 \rightleftarrows 2NO_2$ medium at room temperature and atmospheric pressure. A 70% increase in weight is attained after 5 h under static conditions and after 3 h under dynamic conditions.[51] The changes in the rate of $(UO_3)_{am}$, the results of chemical analysis, and the results of spectroscopic studies on the product indicate that the latter is NTN. Treatment of the kinetic curves[51] yielded n close to two, which shows that the initial stages of the process take place under kinetic conditions. As the reaction product accumulates on the oxide surface, the process slows down and passes to the diffusional region (n = 0.5). With increase in temperature, the reaction also slows down. Fig. 4 illustrates the variation of the weight of the uranium trioxides with the temperature of the dissociating system for a contact time of 5 h. Curve *2* corresponding to the equilibrium process is shown for comparison. It is seen from Fig. 4 that, under equilibrium conditions, the increase in weight reaches 20–70% in the temperature range 293–423 K, after which $\Delta m/m$ falls sharply to zero. The inflections at 423 K were observed also on curves *1* and *3* and their positions are correlated with the contents of NO_2 and N_2O_4 in the gas phase. The degree of conversion of γ-UO_3 is appreciable after 5 h only close to room temperature, while at higher temperatures α did not exceed 1%.

The apparent activation energy E_A for the formation of NTN from $(UO_3)_{am}$ in the temperature range 293–423 K at atmospheric pressure, calculated by several independent equations,[53] amounted to −8.11 ± 0.83 and −7.90 ± 0.83 kJ mol^{-1}.[51] Negative values of E_A were obtained also for the reaction of sodium and potassium peroxides with the dissociating system.[54,55]

Similarly to the observation for liquid N_2O_4, the rate of reaction of gaseous N_2O_4 with $(UO_3)_{am}$ depends on the method of preparation of amorphous uranium trioxide. $(UO_3)_{am}$ specimens with specific surfaces of ~25, 10, and 5 m^2 g^{-1}, obtained by heating $UO_4.2H_2O$ at 623, 673, and 723 K, are converted into NTN after 0.5, 6, and 24 h respectively.[52]

The reactivities of other modifications of uranium trioxide in relation to the $N_2O_4 \rightleftarrows 2NO_2$ system vary in the sequence γ-UO_3 < ε-UO_3 < $(UO_3)_{am}$ and are correlated with their specific surfaces[52] (S_{sp} = 0.9, 2.8, and 9.7 $m^2\ g^{-1}$).

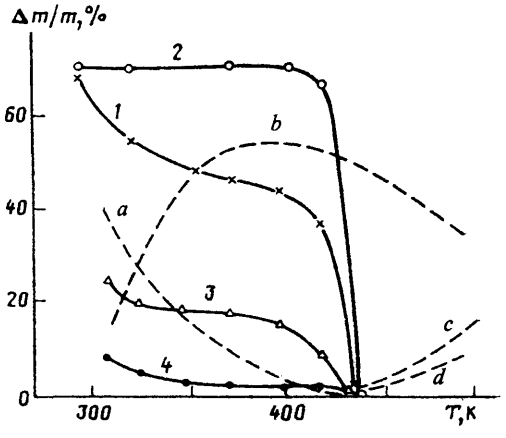


Figure 4. Weight change curves for $(UO_3)_{am}$ (curves *1* and *2*), ε-UO_3 (curve *3*), and γ-UO_3 (curve *4*) in gaseous dinitrogen tetroxide as a function of temperature at p = 0.1 MPa; contact time 5 h except for curves *1*, *3*, and *4*; *2*, specimens maintained under given conditions until the attainment of constant weight; the temperature variation of the composition of the gas phase is shown by dashed curves: *a*, N_2O_4; *b*, NO_2; *c*, NO; *d*, O_2.

The weight of uranium trioxides (Fig. 4) does not change after prolonged contact with the dissociating system at temperatures in the range 423–723 K and there is also no change in the X-ray diffraction patterns of the oxides. This constitutes the difference between the behaviour of uranium trioxides on contact with the dissociating system and that of alkali and alkaline earth metal oxides[56–61] and a series of transition and lanthanide oxides,[52,63] which form nitrides at temperatures above 423 K and the latter are stable in the range 473–673 K.

Starting from temperatures in the range 773–823 K, uranium trioxides in the $2NO_2 \rightleftarrows 2NO + O_2$ medium lose up to 0.5% of their weight and crystallise in the form of a new phase, which was identified as $UO_{2.9}$,[29,64] while in the temperature range 873–1073 K a further weight loss is observed (by 1.8%) and U_3O_8 is formed. In contrast to $(UO_3)_{am}$, ε-UO_3 and γ-UO_3 are converted into U_3O_8, bypassing the $UO_{2.9}$ formation stage.[52]

The nature of the interaction of uranium oxides with the dissociating system in the range 423–723 K is probably determined by the properties of the intermediate products of the decomposition of NTN and in the first place of anhydrous uranyl nitrate.[16–18,37,65–69]

Vibrational spectroscopic data indicate a complex structure of anhydrous $UO_2(NO_3)_2$. The vibration frequencies $\nu_3(UO_2^{2+})$ in this compound are represented by an intense band with three maxima at 990, 980, and 965 cm^{-1}. The fully symmetrical $\nu_1(UO_2^{2+})$ vibration is manifested in the Raman spectrum by doublet bands at 903 and 895 cm^{-1}, one of the components of which (at 895 cm^{-1}) is active in the IR spectrum. The absorption of the nitrate groups in the compounds is distinguished by the greatest complexity. Simultaneously with the presence of doublet bands corresponding to the symmetry point group C_{2v} (1635, 1616 and 1235, 1220 cm^{-1}), the spectrum contains vibrations characteristic of the NO_3^- ion (1381 and 1414 cm^{-1}, Table 4). It has been suggested[37] that the structure of anhydrous uranyl nitrate probably includes at least two types of non-equivalent nitrate groups, the bands at 1414, 1381, 1235, 1220, 1635, and 1616 cm^{-1} belonging to vibrations of the test compounds and not being a result of the interaction of the substance with the material of the filler and hydrate impurities, as suggested by Vdovenko et al.[70]

Table 4. Vibrational frequencies of anhydrous uranyl nitrate.[37]

IR	Raman	Assignment	IR	Raman	Assignment
1635	—		895	903	
1616	1609		—	895	$\nu_1(UO_2^{2+})$
1450	—	ν_{as}(N=O)	798	—	
1440	—		780	—	
1414	—		756	764	$\delta(NO_3^-)$
1381	—		722	724	
1345	—		689	—	
1235	1255	ν_s(N=O)	265	—	
1220	—		255	255	$\nu_2(UO_2^{2+})$
1062	1062		235	215	
—	1010	ν(N=O)	210	199	ν(U—NO_3)
990	—		187	179	δ(U—O—U)
980	—	$\nu_3(UO_2^{2+})$	—	168	
965	—				

According to structural data,[71] discontinuous ("island type") packing with a bidentate mode of addition of nitrate groups is most characteristic of uranyl nitrate complexes of the type $M[UO_2(NO_3)_3]$ and $UO_2(NO_3)_2.2L$. The coordination number of the UO_2^{2+} ion in such compounds is six. The structure of anhydrous uranyl nitrate has been represented[65,66] by a tetragonal bipyramid with equivalent NO_3^- groups and a coordination number of UO_2^{2+} equal to four. It was shown above that this structure of anhydrous uranyl nitrate is inconsistent with the observed IR absorption of UO_2^{2+} and nitrate groups and also with the results of structural analysis. Apart from bidentate binding, in the test compounds there is probably also bridge type binding of nitrate groups, which is fairly well known for other metal nitrates.[72]

Although anhydrous $UO_2(NO_3)_2$ is formed on heating NTN, the results of different workers concerning the temperature ranges and mechanisms of the decomposition of these substances are different.[16–18,67] In particular, it has been claimed[18] that $UO_2(NO_3)_2$ is formed only within the narrow temperature range 436–438 K and that it decomposes to UO_3 in a single stage, while in another study it was assumed[16] that the formation of UO_3 is preceded by a series of intermediate stages with formation of the polymeric oxonitrates $U_2O_5(NO_3)_2$, $U_3O_8(NO_3)_2$, and $U_4O_{11}(NO_3)_2$.

The thermal stability of NTN has been investigated[37] under different atmospheres: in air, in an inert gas stream, *in vacuo*, and in the $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ medium. There are three endothermic effects at 443, 543, and 833 K on the differential thermal analysis

(DTA) curve. The first effect corresponds to the removal of nitrogen dioxide and the formation of anhydrous $UO_2(NO_3)_2$:

$$NO[UO_2(NO_3)_3] \rightarrow UO_2(NO_3)_2 + 2NO_2. \quad (11)$$

Uranyl nitrate is stable within the relatively narrow temperature range 443–473 K, above which it begins to decompose to UO_3. Special experiments involving treatment with acetone of the heat-treatment products obtained at 523, 543, and 573 K [73] (to separate the soluble uranyl nitrates from UO_3) revealed that the $U:NO_3^-$ ratio in the wash solution was 1:2, while the solid residue was UO_3. Thus NTN decomposes in a single stage with formation of uranium trioxide:

$$2UO_2(NO_3)_2 \rightarrow 2UO_3 + 4NO_2 + O_2. \quad (12)$$

In the temperature range 823–873 K, the trioxide UO_3 loses 1.9% of its weight and is converted into U_3O_8.

It has been shown[73] that $NO[UO_2(NO_3)_3]$ decomposes to uranyl nitrate in the temperature range 403–453 K in the kinetic region and takes place from the surface into the bulk of the NTN particles. The process activation energy is ~104.5 kJ mol^{-1}. In contrast to NTN, anhydrous uranyl nitrate decomposes in the diffusional-kinetic region with an activation energy of ~133.9 kJ mol^{-1}. The activation energy E_A for the decomposition of anhydrous uranyl nitrate, quoted by Klavsut',[73] is higher than the value of E_A obtained by Ondrejcin and Garrett[67] and amounts to 98.3 kJ mol^{-1}.

In the gaseous dissociating dinitrogen tetroxide at a pressure of 0.1 MPa, the thermal decomposition of $NO[UO_2(NO_3)_3]$ begins at 453–463 K. With increase in the pressure of a dissociating system, the stability of NTN rises and the limits of its stability at pressures of 0.5, 2, and 10 MPa shift to 503, 523, and 573 K. It has also been observed that NTN decomposes in the dissociating system to UO_3, bypassing the stage involving the formation of anhydrous uranyl nitrate. The presence of the latter has not been detected from the Raman spectra and from the diffraction patterns of the product maintained in the dissociating system at a temperature above 573 K and a pressure in the range 2–10 MPa.[50–52]

On decomposition of NTN and of anhydrous uranyl nitrate, the formation of intermediate oxonitrates as well as uranyl nitrates was not observed. They are not formed in the above heterogeneous processes and can be synthesised only by ligand substitution reactions.[74]

When U_3O_8 and UO_2 are treated with gaseous dinitrogen tetroxide at room temperature under dynamic conditions, the change in weight after 5 h is ~15%, while under static conditions the weight increment reaches 10% only after 24 h. The process then slows down and under static conditions its completion requires approximately half a year. The interaction with UO_2 is even slower. Under dynamic conditions, the increase in weight after 24 h is only 3%. The reaction is completed after 8–10 months. The changes in the weight of U_3O_8 and UO_2 are 73 and 80% respectively, which corresponds to the formation of NTN. The kinetics of the reactions depend on the specific surfaces of the initial specimens: U_3O_8 with S_{sp} = 13.6 m^2 g^{-1} is converted into $NO[UO_2(NO_3)_3]$ after 10 and 15 days at 293 K under dynamic and static conditions, while $(UO_2)_{act}$ is converted after 2 and 3 days respectively (S_{sp} ~ 80 m^2 g^{-1}).

There are two sections on the kinetic curves for the interaction of U_3O_8 and UO_2 with the gaseous dissociating $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ system: the initial sharp increase in the degree of conversion and the subsequent retardation of the process (Fig. 5). The value of n along the initial sections for U_3O_8 is 1.6–2.0, which corresponds to the occurrence of the process in the kinetic region. The apparent activiation energy for the formation of NTN from U_3O_8 is -10.59 ± 1.84 kJ mol^{-1} and is close to that for UO_3. As NTN accumulates on the surface of the oxide, the reaction occurs in the diffusional region (n = 0.1–0.5).

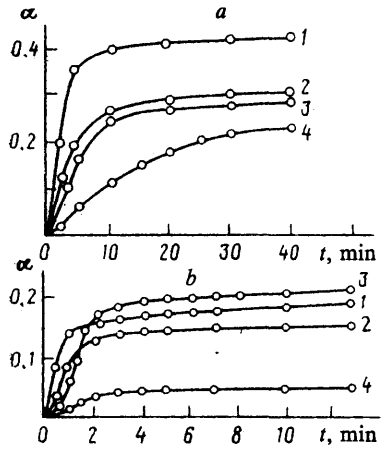


Figure 5. Variation of the degree of conversion of U_3O_8 (*a*) and UO_2 (*b*) in gaseous dinitrogen tetroxide at different temperatures (K): *1*, 293; *2*, 323; *3*, 373; *4*, 423.

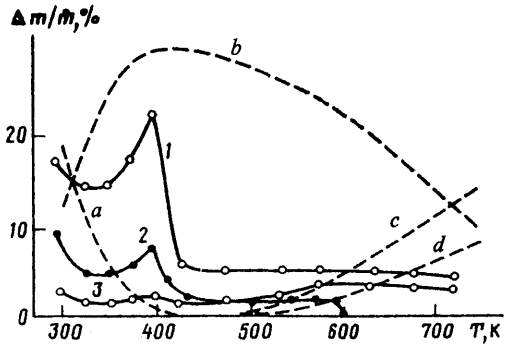


Figure 6. Weight change curves for $(UO_2)_{act}$ (curve *1*), U_3O_8 (curve *2*), and UO_2 (curve *3*) in gaseous dinitrogen tetroxide as a function of temperature at p = 0.1 MPa in the course of 5 h; the temperature variation of the composition of the gas phase is shown by dashed curves: *a*, N_2O_4; *b*, NO_2; *c*, NO; *d*, O_2.

In contrast to uranium trioxides, the temperature variation of the degrees of conversion of U_3O_8 and UO_2 is complex. When the plot of $\Delta m/m$ against T in the range 293–423 K is analysed, the presence of a very intense maximum for $(UO_2)_{act}$ and a less intense one for U_3O_8 at 393–403 K is striking (Fig. 6).[50,51] The increase in the reactivity of uranium oxides in which the oxidation state of the metal is less than 6 at 392 K is determined by the formation of

ε-UO_3 during the reaction. Its appearance has been established by X-ray diffraction. After the uranium oxides had been kept in dinitrogen tetroxide at the temperature indicated, they were treated with acetone to remove uranyl nitrates. It was found that, apart from the peaks characteristic of the initial oxides, the ε-UO_3 diffraction maxima are present on the diffraction patterns of the specimens. The presence of ε-UO_3 as an intermediate phase in the products of the reaction of U_3O_8 and UO_2 with the dissociating system shows that they react in two stages: the oxidation of U_3O_8 and UO_2 to ε-UO_3 and the subsequent formation of NTN. With increase in temperature, the rate of the first process rises and that of the second falls. The formation of the intermediate oxide ε-UO_3, which is more reactive than UO_2 and U_3O_8, accelerates the formation of NTN and induces the appearance of a maximum on the curves for the temperature variation of α. At temperatures above 423 K and a pressure of 0.1 MPa, the formation of NTN ceases as a consequence of its thermal decomposition and a sharp fall in weight is observed on the curves (Fig. 6).

In the range 453–523 K, the main product of the reaction of U_3O_8 with the dissociating system is ε-UO_3. The kinetic curves for the conversion of U_3O_8 into ε-UO_3 obtained by the present authors[51] show that the process is accelerated as the temperature rises. They are described satisfactorily by a first-order reaction equation: $\alpha = 1 - \exp(-kT)$; the activation energy is $E_A = 79.5 \pm 0.88$ kJ mol^{-1}. At temperatures above 623 K, no changes in the weight of U_3O_8 are observed although ε-UO_3 has been stated[27,75] to be stable up to 723 K. This is probably due to the phase transition from orthorhombic U_3O_8 to U_3O_8 with a hexagonal structure[76] whose properties are similar to those of hexagonal ε-UO_3.[77]

In the case of UO_2, in the range 453–523 K an increment in weight of ~1% has been observed, but the X-ray diffraction patterns of the specimens remain unchanged under these conditions.[50] This is evidence for the insertion of oxygen into the cavities of the fluorite structure of uranium dioxide with formation of the non-stoichiometric compounds UO_{2+x}, where $x = 0.20-0.34$.[78] At 623 K and above, the main phase is U_3O_8.

With increase in pressure in the system, the rate of formation of NTN increases appreciably. Thus $(UO_3)_{am}$ is fully converted into NTN after 5 h at 0.5 MPa and temperatures in the range 323–473 K and after 1 h at a pressure of 10 MPa and 473 K. The temperature range corresponding to the stability of NTN shifts at the same time to the region of higher temperatures.[52] NTN remains stable up to 503 K at a pressure of 0.5 MPa and up to 573 K at 10 MPa. The curves for the variation of the weight of U_3O_8 and UO_2 with the pressure of the dissociating system exhibit a maximum similar to that observed at atmospheric pressure.[50,51] However, the position of the maximum, corresponding to the formation of ε-UO_3, is displaced towards higher temperatures. The reactivity of uranium oxides in relation to the dissociating system follows the same sequence as at atmospheric pressure: $(UO_3)_{am} > \varepsilon\text{-}UO_3 > \gamma\text{-}UO_3 > U_3O_8 > UO_2$.[52] Consequently, with increase in the pressure of the dissociating system, the mechanisms of the reactions with uranium oxides do not change and only the rate of reaction and the thermal stability of NTN increase significantly. Above 573 K, NTN is not formed from uranium trioxides even at a pressure of 10 MPa.

In contrast to the reactions at atmospheric pressure, at $p > 0.5$ MPa in the temperature range 573–723 K the oxides $(UO_3)_{am}$ and ε-UO_3 undergo a phase transition with formation of the most stable modification γ-UO_3, which loses oxygen at a temperature above 773 K with formation of the oxide $UO_{2.9}$ and then U_3O_8.

γ-UO_3 is obtained under the same conditions as U_3O_8. The phase having the composition $UO_{2.9}$ is formed during the oxidation of U_3O_8 at temperatures in the range 623–723 K at a pressure of 0.5 MPa. In the temperature range 723–873 K and in the pressure range 0.2–10 MPa, uranium trioxides and UO_2 are converted into U_3O_8. However, at pressures above 2 MPa in the temperature range 573–673 K, the γ-UO_3 phase was detected in reaction products. It was absent at the same temperatures and atmospheric pressure.

IV. Interaction of uranium oxides with N_2O_4–organic solvent mixtures

We noted above that liquid N_2O_4 does not interact with the majority of metals. In order to achieve such reactions, mixtures of liquid N_2O_4 with organic solvents are employed. The chemical behaviour of dinitrogen tetroxide is associated with the characteristics of its electronic structure. Each atom in N_2O_4 has *p* orbitals perpendicular to the plane of the molecule and forming a system made up of six π molecular orbitals in which 12 electrons can be accommodated. N_2O_4 has only eight electrons in its molecular orbitals, as a result of which it exhibits the properties of an acceptor capable of accepting two pairs of electrons. The tetroxide N_2O_4 does not show a tendency to react with metals. On the other hand it forms readily molecular complexes with electron-donating solvents.[79] It has been noted[80] that, as the electron-donating properties of the solvent are enhanced, the absorption maximum $\lambda_{max}(N_2O_4)$ in the range 330–340 nm diminishes and the extinction coefficient of the complex formed increases. According to Solov'ev et al.,[81] in weak organic bases at high concentrations of N_2O_4 the latter exists mainly as undissociated molecules. Only at low N_2O_4 concentrations does the homolytic dissociation $N_2O_4 \rightleftarrows 2NO_2$ occur and the concentration of NO_2 becomes comparable to that of N_2O_4. The thermodynamic parameters of the homolytic dissociation reactions of N_2O_4 in CS_2, $CHCl_3$, CCl_4, $SiCl_4$, and n-hexane depend little on the nature of the solvent.[81] On the other hand, in strong organic bases the heterolytic dissociation $N_2O_4 \rightleftarrows NO^+ + NO_3^-$ takes place.[79]

The introduction of an organic solvent increases the dielectric constant of N_2O_4, promoting the formation of ion pairs. The processes can be represented by the following scheme:

$$m\,L + N_2O_4 \rightleftharpoons (L)_m \cdot N_2O_4 \rightleftharpoons [L_mNO^+]\,[NO_3^-]. \qquad (13)$$

Since the N_2O_4 molecule can accept two electron pairs in its orbitals, *m* is as a rule equal to two.

Adducts of the nitrates of the corresponding metal with N_2O_4 or with the solvent are formed in mixed solvents: $M(NO_3)_2.N_2O_4$ and $M(NO_3)_2.nL$. The former complexes are usually nitrosonium compounds in the solid phase, like nitrosonium trinitratouranylate.

In the reactions of metallic uranium and its oxides with mixtures of N_2O_4 and organic solvents, the solvent was evaporated in order to obtain the final products. As a result, NTN was formed from mixtures of N_2O_4 with nitromethane and nitrobenzene whereas adducts of uranyl nitrate with two molecules of the organic base, namely $UO_2(NO_3)_2.2L$, were obtained with solvents such as CH_3CN, $(CH_3)_2CO$, $(C_2H_5)_2O$, $(CH_3)_2NCOH$, and $(CH_3)_2SO$.[14,16,82]

We may note that the formation of uranium(IV) compounds was not observed as a result of the reaction, only uranyl complexes being detected in the reaction products. Thus, as has been observed for gaseous and liquid N_2O_4, in mixtures of N_2O_4 with organic solvents the

first stage of the reaction is the oxidation of uranium to the hexavalent state:

$$U + 2\,[NO^+]\,[NO_3^-] \rightarrow UO_2^{2+} + 2\,N_2O_3. \quad (14)$$

Since NTN is formed only in the case of nitromethane and nitrobenzene, its formation cannot be accounted for by the high dielectric constant of the solvent, which is responsible according to Addison and co-workers,[82-84] for the heterolytic dissociation of N_2O_4. Indeed, adducts formed by the addition of two molecules of the solvent to uranyl nitrate are obtained in the reactions with acetonitrile, dimethylformamide, and dimethyl sulphoxide, which have higher dielectric constants (ε = 38.0, 36.1, and 44.5) than nitromethane and nitrobenzene (35.9 and 34.8 respectively).

The formation of the adducts agrees well with the increasing electron-donating capacity of the solvent. On passing from nitromethane and nitrobenzene to stronger bases, i.e. acetone, diethyl ether, dimethylformamide, and dimethyl sulphoxide, their donor numbers increase correspondingly: 2.7, 4.4, 17.0, 19.2, 26.6, and 29.8.[85] Thus the complexes $UO_2(NO_3)_2.N_2O_4$ for solvents having a low electron-donating capacity probably exist in solutions of N_2O_4. Their composition is better reflected by the formula $UO_2(NO_3)_2.N_2O_4$ than by $UO_2(NO_3)_2.2NO_2$, because the degree of the dissociation $N_2O_4 \rightleftarrows 2NO_2$ in liquid N_2O_4 is 140–500 times smaller than in the gas phase owing to the "cage" effect of the liquid.[86] In solution, the stability of the complex is apparently achieved via the stable isomer O_2N-NO_2,[87] which behaves as a bidentate neutral ligand. As the complex passes to the solid phase, the stability of this isomer diminishes and it is converted into the $ON-NO_3$ isomer with formation of a nitrosonium compound. The equilibrium in the heterolytic dissociation of liquid N_2O_4 has been displaced[88-91] by adding alkylammonium nitrates or nitrosyl chloride.

In terms of its electron-donating properties, N_2O_4 is probably close to nitrobenzene and stronger bases can compete with N_2O_4, displacing it from the inner coordination sphere of UO_2^{2+}.

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Layered compounds of alkali metals in graphite in fine organic synthesis

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ABSTRACT. The review deals with the use in fine organic synthesis of layered compounds of graphite with alkali metals as catalysts and reactants. The high reactivity of these compounds in alkylation, polymerisation, reduction, and certain other reactions is demonstrated.

The bibliography includes 76 references.

Contents

I. Introduction 738
II. Preparation of layered compounds of graphite with alkali metals 738
III. The structure of layered compounds of graphite with alkali metals 739
IV. Chemical properties 739

I. Introduction

As enhanced interest in non-traditional compounds with unique properties is constantly manifested in chemistry. An expansion of the range of practical applications of layered compounds of graphite (LCG) with unusual physicochemical properties has been noted recently. For example, LCG, which are good electrical conductors, can be used as cathodic materials in the construction of chemical current sources and also as systems designed for the storage of thermal energy.[1] The application of LCG as additives improving the physicochemical properties of certain varieties of abrasive materials and powdered alloyed steels as well as raw materials for the preparation of new carbon materials with controllable physicochemical properties appears promising.[2] It is of interest to use LCG as catalysts and reactants in various chemical processes, for example, in the synthesis of ammonia and artificial diamonds[3,4] and also in fine organic syntheses.[3]

There exist several reviews devoted to the application of LCG with alkali metals in organic reactions.[5–8] The review of Novikov and Vol'pin[5] is devoted to the preparation of LCG with alkali metals, their structure, and their thermodynamic and physicochemical properties. It includes a brief list of the simplest reactions with participation of these compounds. Boersma's review[6] deals with a limited range of organic reactions: dimerisation, isomerisation, and polymerisation of unsaturated aliphatic compounds catalysed by alkali metals in graphite. Inclusion compounds of graphite with various substances (acids, salts, alkali metals, etc.) and their use in organic chemistry have been described in two other reviews[7,8] without a detailed consideration of the reactions occurring in the presence of LCG with alkali metals.

In view of the foregoing, it appeared useful to subject the characteristic properties of LCG with alkali metals to a comprehensive consideration, concentrating attention on the use of these unusual compounds in synthetic organic chemistry.

II. Preparation of layered compounds of graphite with alkali metals

Three main methods of preparation of LCG with alkali metals have been described. In our view, the most convenient and most widely used is the method involving the joint heating of the alkali metal and graphite,[5,9–11] which is usually carried out in a stream of an inert gas. LCG with K, Rb, and Cs can be readily obtained by this procedure at temperatures from 100 to 500 °C. The composition of the layered compounds obtained varies from C_8M to $C_{60}M$ (M = metal). For a long time, it was impossible to synthesise by this procedure the analogous compounds of graphite with lithium or sodium, but ultimately LCG having the composition C_nNa, where $n = 60-68$, and C_nLi, where $n = 4-72$, were obtained.[5] The method of preparation of LCG with potassium or lithium under pressure (2.0–8.0 GPa, 200–300 °C) made it possible to synthesise inclusion compounds with an increased metal content: $C_{2.00-2.5}Li$ and $C_{4.0-4.5}K$.[12,13]

Yet another method of synthesis of LCG with alkali metals is based on the reaction of graphite with the metals in solution.[5,11,14,15] Polar solvents of the type of ammonia, 1,2-dimethoxyethane, amines, hexamethylphosphoramide, etc. are usually employed and the reaction is carried out at temperatures from −50 to −100 °C. Together with alkali metals, the solvent is also incorporated in graphite in this instance.[5,15] The amount of incorporated solvent depends on the size of its molecules. For example, in the preparation of LCG with potassium in ammonia, we have the ratio $K:NH_3 = 1:2$, while in the case where pyridine or methylamine are used the corresponding ratio is 1:1.

The third method of preparation of the LCG considered provides for the interaction of graphite with solutions of radical-anions derived from aromatic compounds (biphenyl, naphthalene, phenanthrene, etc.)[5] in accordance with the following general scheme:

$$ArH^{-}M^{+} + \text{graphite} \rightleftarrows ArH + \text{graphite}^{-}M^{+}(Solv)(ArH). \quad (1)$$

The equilibrium amount of alkali metal incorporated in graphite is independent of the nature of the radical-anion, which does, however, influence the rate of equilibration. For example, equilibrium (1) is more rapidly established in the reaction with biphenyl than with naphthalene. This is probably associated primarily with the electrochemical potentials of aromatic compounds. Thus the reduction potential of naphthalene in relation to biphenyl is +0.9 V.[5]

The rate of incorporation of the metal in graphite varies in the course of the reaction. For example, when a solution of naphthalenepotassium is used, 80% of potassium is incorporated in the first 5 h, while the incorporation of the remaining 20% requires a further 45 h. Apart from the alkali metal, the solvent and small amounts of the aromatic compound can also be incorporated in graphite in this method of preparation.[5]

III. The structure of layered compounds of graphite with alkali metals

The carbon atoms in graphite form planar network structures with hexagonal cells of the type of benzene rings. Each carbon atom in this system has a free π-electron in the p orbital located at right angles to the molecular plane. The parallel networks of carbon atoms are linked by weak van der Waals forces, and not chemical bonds, which permits the incorporation of various compounds into the interlayer space. The graphite layers are then moved apart and LCG are formed in which there are no strong vertical bonds, i.e. bonds between the incorporated compound and the carbon atoms of graphite.

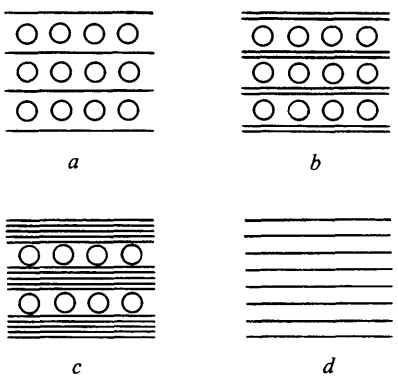
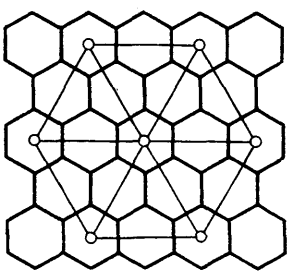


Figure 1. Disposition of the layers of graphite and alkali metal atoms in intercalation compounds: *a*, 1st stage LCG (C_8M); *b*, 2nd stage LCG ($C_{24}M$); *c*, 5th level LCG ($C_{60}M$); *d*, graphite.

In terms of their structure, LCG with alkali metals can be divided into five stages[5,10,11] (Fig. 1). In the first stage, the layers of metal and graphite alternate and the metal atoms form a monatomic layer equidistant from the nearest carbon layers. In the metallic layer, a network is created in which the distance between the atoms is 4.30 Å (Fig. 2). In the second stage ($C_{24}M$), each metal layer is followed by two graphite layers, while in fifth stage compounds ($C_{60}M$) each metal layer is followed by five graphite layers. The thickness of the filled graphite layer in LCG with the same metal is the same for compounds corresponding to any stage and depends solely on the size of the incorporated metal. The interplanar distances are 3.73, 4.50, 5.33, 5.68, and 5.94 Å for Li, Na, K, Rb, and Cs compounds respectively. On passing to higher stages, not only does the number of carbon layers per metal layer increase but there also is a change in the structure of the metal layer itself. In the compounds C_8M, the metal atoms are arranged in a triangular network (Fig. 2), while on passing to the second stage they are rearranged to a hexagonal network, i.e. the central metal atom is displaced from the plane of the lattice (Fig. 2).



○alkali metal atom

Figure 2. Disposition of alkali metal atoms in intercalation compounds in relation to the carbon matrix of graphite.

The structure of LCG containing, apart from alkali metals, also the solvent is similar to that of compounds formed in the absence of the solvent. Solvent molecules are distributed in the same layer as the metal atoms. The distance between the graphite layers (the thickness of the filled layer) in the intercalation compounds consists of the distance between the same layers in the unfilled graphite (3.35 Å) and the thickness of the layer of solvated ions. The latter quantity is 6.6 Å for ammonia, 6.9 Å for methylamine, and 8.5 Å for ethylenediamine. The thickness of the filled layer is independent of the nature of the metal and the stage of the compound but does not depend on the molecular size of the solvent.

The question of the nature of the bond with alkali metals in the LCG is very important. The model according to which the layered compounds consist of "metal-like" carbon networks of graphite and layers of M^+ metal ions appears most likely. The cations are formed as a result of the transfer of one electron from the metal atoms to the conductivity band of the neighbouring graphite layer. Consequently, the alkali metals in LCG are fully ionised and the formation of a bond between the alkali metal and the carbon network of graphite is determined by the electrostatic interaction of the positively charged metal ions with the free electrons of the conductivity band of the neighbouring graphite layers.[10,11,16,17]

IV. Chemical properties

1. Reactions with gases and proton-donating compounds

The layered compounds of graphite with alkali metals are pyrophoric and ignite in air. They are therefore usually obtained and stored under an inert atmosphere (helium, argon). Compounds of the type C_8M (M = K, Rb, Cs) can be stored under a nitrogen atmosphere (Table 1).[6] Compounds of the type $C_{24}M$ sorb virtually all the gases listed in Table 1, including argon, but excluding helium and neon,

while the compounds C_8M do not sorb any of the gases. This difference is probably due to the fact that the density of alkali metal atoms in C_8M is approximately 1.5 times greater than in $C_{24}M$. This prevents the incorporation of gas molecules into the interlayer space of compounds of the type C_8M.

LCG with alkali metals can be stored not only under an inert atmosphere but also in dry solvents (diethyl ether, pentane and others). The reactivity of the inclusion compounds is maintained for a long time under these conditions.

Table 1. The ratio of the number of gas molecules absorbed by LCG to the number of intercalated alkali metal atoms (at −67 to −190 °C).[6]

LCG	He	Ne	Ar	N_2	H_2, D_2	CH_4
$C_{24}K$	nil	nil	nil	0.70	2.10	nil
$C_{24}Rb$	nil	nil	1.20	1.00	2.05	0.90
$C_{24}Cs$	nil	nil	1.40	1.30	2.00	1.20
C_8M (M = K, Rb, Cs)	nil	nil	nil	nil	nil	nil

Table 2. The interaction of the compound C_8K with certain oxides and oxygen.[6]

Oxide	Reaction temperature, °C		Products
	start	end	
O_2	25	120	graphite + α-KO_2
N_2O	120	200	graphite + α-KO_2 + $N_2\uparrow$
NO*	25	250	graphite + Q** + ?
NO_2*	25	100	graphite + KNO_2 + Q
SO_2	25	300	graphite + K_2SO_4 + $S\downarrow$
CO_2	120	400	graphite + K_2CO_3 + $CO\uparrow$
CO	200	500	graphite + K_2CO_3

* Exothermic process.

** Q is the amount of heat evolved during the reaction.

LCG with alkali metals can react with various oxides and oxygen (Table 2).[6] These reactions, which usually begin at room temperature, proceed with evolution of heat. This normally results in the formation of two-phase systems consisting of graphite and a finely dispersed inorganic salt. Attention should be drawn to the fact that, in the interaction of C_8K with O_2 and N_2O, the α-form of KO_2 is formed. In the absence of LCG, it is usually obtained at temperatures below −75 °C. At room temperature, the β-form of this compound is stable.

The compound C_8K is capable of absorbing hydrogen even at room temperature.[18,19] On heating, the reaction is accelerated with formation of products having the composition C_8KH_x, where x depends on the reaction temperature and reaches a limiting value of 0.67. The compounds C_8Rb and C_8Cs are more stable in relation to hydrogen than C_8K. The maximum value of x in C_8RbH_x, attained at 60 °C, is 0.05; C_8Cs begins to react with hydrogen above 150 °C.

Gaseous chlorine, bromine, and iodine react very vigorously with C_8K and C_8Cs, forming finely dispersed metal halides.[20] In this case, the structure of the LCG is fully disrupted and, according to X-ray diffraction data, the final specimen consists of two phases — graphite and the metal halide.[6,20]

When LCG with alkali metals (K, Rb, Cs) are acted upon by water, the following reactions take place:[21,22]

$$C_8M + H_2O \rightarrow C_8H + MOH, \quad (2)$$

$$C_8M + H_2O \rightarrow 8C + MOH + {}^1/_2H_2. \quad (3)$$

Since 0.5 mol of hydrogen should be evolved in reaction (3) per mole of C_8M, while in the experiment where water is added to LCG with alkali metals only 0.01−0.08 mol is evolved, one may conclude that reaction (2) predominates in this process, the remaining hydrogen being consumed in the hydrogenation of graphite. Under the experimental conditions, it is difficult to separate the contributions of reactions (2) and (3). At any rate in the reactions of LCG containing alkali metals with water, the evolution of H_2 has always been detected,[5,21,22] the amount of such hydrogen depending greatly on the particle size of the graphite employed.[23] It has been suggested that, when LCG with alkali metals are acted upon by water, only the positively charged metal layer interacts with water, while the graphite layer represents an inert macroanion, which does not react with water, forming inclusion compounds with the latter.[24]

Hydrogen is also evolved when ternary compounds of the type graphite/alkali metal/solvent are treated with water. The solvents employed are tetrahydrofuran (THF)[21,25] or ammonia.[26]

The interaction of alkali metal intercalants in graphite with alcohol proceeds similarly, but in this case the corresponding alkoxides are formed in addition to hydrogen.[21]

A detailed investigation of the reaction of the potassium intercalant in graphite with various alcohols and diols[27] is important because compounds with an OH group are extremely common in synthetic organic chemistry. When the LCG with potassium is acted upon by an alcohol or diol, both the evolution of hydrogen and the formation of the corresponding alkoxide are observed.

The amount of potassium extractable from the intercalant in the form of the alkoxide depends on the structure of the alcohol (diol), the type of intercalant, and the nature of the solvent used to extract the alkoxide (Table 3). Naturally, with decrease in the content of potassium in graphite, the amount of extractable alkoxide diminishes but not in proportion to the molar content of potassium. For example, after the treatment of the LCG with 2-butanol, cyclohexane extracts from $C_{24}K$ even more potassium alkoxide than from C_8K (36 and 24% respectively). The effectiveness of the solvent used to extract alkali metals from intercalants increases in the sequence cyclohexane ≃ hexane < benzene < THF ≃ dimethoxyethane (DME).[28,29] Monohydric alcohols extract alkoxides more effectively than polyhydric alcohols. Lithium passes to the alcohol phase much less effectively than potassium (by a factor of approximately 2). The most complete extraction of potassium has been observed in THF, where the degree of extraction reaches 60−70% (Table 3). The extraction is hindered by side

reactions occurring when OH-containing compounds interact with LCG which contain alkali metals, namely reactions due to the evolved hydrogen and others.

Table 3. The amount of potassium extracted from LCG by alcohols and glycols (contact time 48 h, 23 °C).[27]

Alcohol (diol)	No. of carbon atoms (n) in C_nK	Degree of extraction of potassium, %		
		by cyclohexane	by benzene	by THF
2-Butanol	8	24	55	67
2-Butanol	24	36	47	64
t-Butyl alcohol	8	20	43	60
t-Butyl alcohol	24	18	40	58
Diphenylmethanol	24	—	20	59
Diphenylmethanol	12*	—	10	27
Decanediol	24	—	2	17
PEG (300)**	24	—	35	50
PPG (400)***	24	—	38	53

* $C_{12}Li$ was used.
** Polyethylene with a molecular weight of 300.
*** Polypropylene with a molecular weight of 400.

It is believed [21] that such reactions do not take place with amines which are less acidic than alcohols. Thus, when cyclohexylamine or pyrrolidinone was added to a suspension of C_8K in THF, hydrogen was not evolved and the colour of the solution did not change.

2. Hydrogenation and reduction reactions

The reducing properties of C_8K were first demonstrated in relation to the reaction of bis(trialkyl phosphite)nickel(2+) dichloride with an excess of trialkyl phosphite, which resulted in the formation of a zerovalent nickel complex—tetrakis(triethyl phosphite)nickel(0).[30]

Treatment with the potassium intercalant in graphite results in the hydrogenation of the double bond in α,β-unsaturated ketones and acids and the formation of a satisfactory yield of the corresponding unsaturated compounds under mild conditions:[31]

$$C_6H_5-CH=CH-CO-CH_3 \xrightarrow[2)\ H_2O,\ 10\ min,\ 25\ ^\circ C]{1)\ C_8K,\ THF,\ [(H_3C)_3Si]_2NH} C_6H_5-CH_2-CH_2-CO-CH_3,$$

(I)

85%

$$R^1-CH=CH-COOH \xrightarrow[2)\ H^+/H_2O,\ 55\ ^\circ C,\ 60-90\ min]{1)\ C_8K,\ THF} R^1-CH_2-CH_2-COOH.$$

R^1	Yield, %
C_6H_5	86
CH_3	85
COOH	89

When type (I) unsaturated ketones were hydrogenated, best results were achieved using a 5:1 mixture of THF and hexamethyldisilazane as the reaction medium.

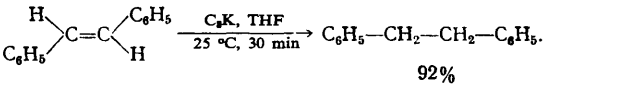
Aromatic Schiff bases are also reduced under mild conditions, affording the corresponding secondary amines:[31]

$$C_6H_5-CH=N-R^1 \xrightarrow[2)\ H_2O,\ 25\ ^\circ C]{1)\ C_8K,\ THF} C_6H_5-CH_2-NH-R^1.$$

The yield was 83% for R^1 = cyclo-C_6H_{11} and 92% for R^1 = t-C_4H_9. On the other hand, α,β-unsaturated esters, such as the ethyl esters of fumaric, geranic and 3-methylbut-2-enoic acids, give rise mainly to dimerisation products under these conditions.[31]

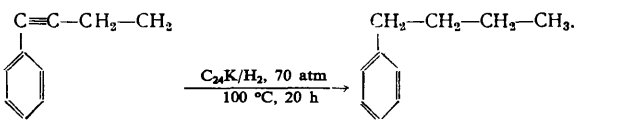
The hydrogenation of mixtures of alkenes, namely oct-1-ene and 1-methylcyclohexene, oct-1-ene and dodec-1-ene, and *cis*-oct-2-ene and 1-methylcyclohex-1-ene in the presence of $C_{24}K$ has been described (70 atm, 100 °C, 20–24 h).[32] The reaction took place most effectively on treating a mixture of oct-1-ene and the dodec-1-ene with the potassium intercalant, whereupon octane and dodecane were formed in equal yields (28% each).

1,2-Diphenylethane has been obtained in 92% yield (70 atm, 100 °C, 60 h) from *trans*-stilbene in benzene on treatment with H_2 and $C_{24}K$. The same yield of 1,2-diphenylethane was achieved on treating *trans*-stilbene with a fivefold excess of C_8K in THF but under milder conditions and without adding hydrogen:[31]



92%

Examples of the hydrogenation of the triple bond are also known. For example, on treatment with $C_{24}K$, 1-phenyl-1-yne is converted into n-butylbenzene in a satisfactory yield:[32]



75%

The reduction of many primary halogenoalkanes on treatment with C_8K has been described:[21]

$$CH_3(CH_2)_{16}CH_2X + C_8K \xrightarrow[30\ min]{25\ ^\circ C} \underset{(II)}{C_{18}H_{38}} + \underset{(III)}{C_{36}H_{74}}. \qquad (4)$$

X	Solvent	Yield, % (II)	Yield, % (III)
Cl	C_5H_{12}	40	—
Cl	$(C_2H_5)_2O$	93	—
Br	THF	38	56
I	$(C_2H_5)_2O$	47	53
I	THF	26	73

In process (4), reduction is the dominant reaction when chloro-derivatives of organic compounds are used, especially in diethyl ether. On passing to bromo- and iodo-derivatives, the Wurtz reaction begins to predominate.

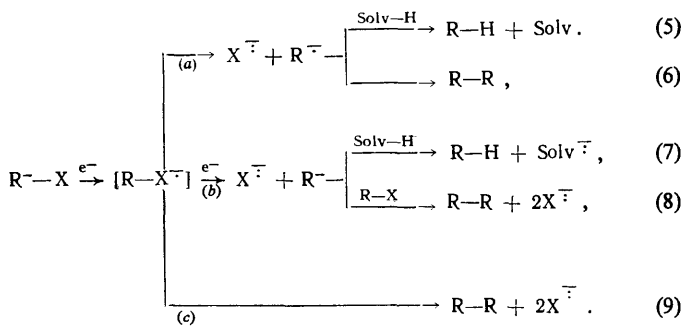
Under these conditions, tosyl derivatives afford mainly alcohols and phenols:[21]

$$R-OTs \xrightarrow[25\ ^\circ C,\ 30\ min]{C_8K,\ THF} R-OH,$$

$OTs = p\text{-}CH_3C_6H_4SO_3$.

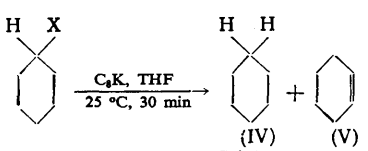
R	Yield, %
$CH_3(CH_2)_{16}CH_2$	95
C_6H_5	61

The mechanism of the reduction of halogenoalkanes by LCG with alkali metals can be represented schematically as follows:



In the first stage, one-electron transfer takes place with formation of a radical-anion, which can react further via several pathways (*a*, *b*, *c*). The heterolytic dissociation of the bond in the radical-anion complex (pathway *a*) results in the formation of a free radical which "abstracts" a hydrogen atom from the solvent Solv-H [reaction (5)] or dimerises [reaction (6)]. At the same time, yet another electron can add to the radical-anion, after which fragmentation (pathway *b*) and reactions (7) and (8) take place. One cannot rule out also the direct dimerisation of the radical-anion via pathway *c* [reaction (9)].

Halogenocyclohexanes are reduced on treatment with C_8K to unsubstituted cyclohexanes or cyclohexenes:[21]

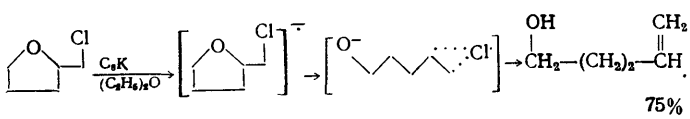


Yield, %

X	(IV)	(V)
Cl	84	15
Br	56	40
I	5	88

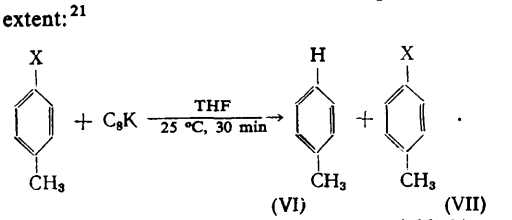
The composition of the products of this reaction is to a large extent determined by the nature of the substituent X. If X = Cl, then the main product is cyclohexane, while for X = I dehydrohalogenation with formation of cyclohexene predominates.

On treatment with LCG with potassium, tetrahydrofurfuryl chloride is converted into pent-4-en-1-ol:[21]



75%

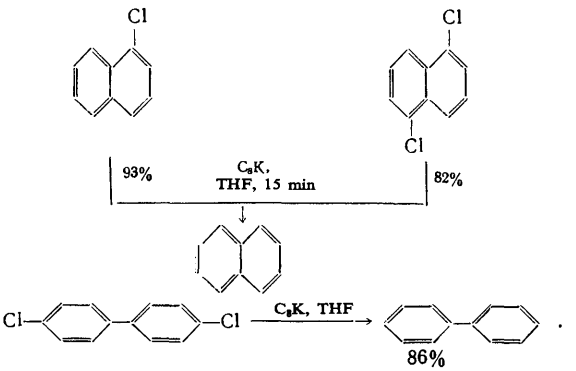
Aromatic halogeno-derivatives are more resistant to the action of LCG with alkali metals and the reduction process takes place to a lesser extent:[21]



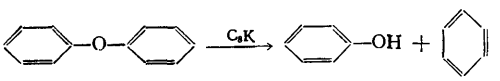
Yield, %

X	(VI)	(VII)
Cl	50	50
Br	48	52

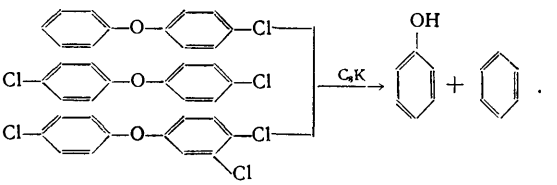
On the other hand, polynuclear aromatic halogeno-compounds, namely 1-chloronaphthalene, 1,8-dichloronaphthalene, or 4,4′-dichlorobiphenyl, afford the corresponding hydrocarbons in a high yield on treatment with C_8K at room temperature:[33]



Examples of the cleavage of the Ar—O—Ar linkage are also described in the same communication:[33]



Reactions involving dehydrohalogenation and the cleavage of the Ar—O—Ar linkage can also take place simultaneously:[33]



On treatment with C_8K, 1,2-dihalogenoalkanes are readily converted into the corresponding alkenes[21] and the double bond formed is not hydrogenated, although, for example, stilbene is hydrogenated quantitatively to 1,2-diphenylmethane under these conditions after 30 min:[31]

$$C_8H_{17}CHBr—HCHBr \xrightarrow[25\ ^\circ C,\ 24\ h]{C_8K,\ THF} C_8H_{17}CH{=}CH_2.$$

94%

The reduction of such double bonds probably requires more severe conditions and the presence of excess hydrogen.[6]

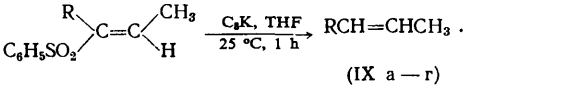
1,2-Disulphonic acid esters of type (VIII) also afford alkenes under these conditions but in a lower yield, because the elimination process is complicated by side reactions:[21]

$$C_6H_{13}\underset{\underset{OMs}{|}}{CH}—\underset{\underset{OMs}{|}}{CH_2} \xrightarrow[25\ ^\circ C,\ 24\ h]{C_8K,\ THF} C_6H_{13}CH{=}CH_2;$$

(VIII) 58%

Ms = SO_2CH_3.

A novel example of the stereoselective reduction in the presence of C_8K of α,β-unsaturated phenyl sulphones to alkenes with the preferential formation of the (*E*)-isomer has been described:[34]

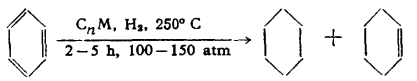


(IX a — r)

R	Yield of (IX), % (*Z*:*E* ratio)
(a) n-C_4H_9	61 (30:70)
(b) n-C_8H_{17}	65 (35:65)
(c) n-$C_{16}H_{33}$	55 (35:65)
(d) $C_6H_5CH_2$	26 (40:60)

If the reduction is carried out in the presence of lithium methylamide, undec-2-ene, with the (*Z*)-isomer predominating (65%), is formed from benzene-2-sulphonylundec-2-ene in 55% yield.[34]

Using potassium intercalants in graphite, it has been possible to achieve the catalytic hydrogenation of benzene and alkylbenzenes under relatively mild conditions:[35]



(X) (XI) (12)

Yield, %

C_nM	(X)	(XI)
C_8K	79.7	—
$C_{24}K$	86.0	—
K/C	37.0	—
$C_{24}Li$	14.0	—
K	2.7	87.0

The most effective catalysts of this process are C_8K and $C_{24}K$. Metallic potassium deposited on activated charcoal with a specific surface of 890 $m^2 g^{-1}$ has an appreciably lower catalytic activity than the potassium intercalants (the specific surfaces of C_8K and $C_{24}K$ are less than 10 $m^2 g^{-1}$). LCG with lithium is even less active. In the presence of metallic potassium, the main reaction product is cyclohexene.

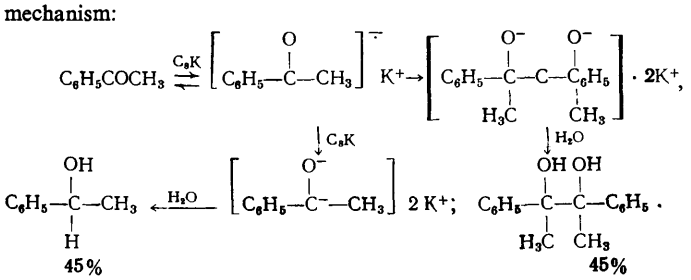
Toluene and propylbenzene can also be reduced under analogous conditions on treatment with $C_{24}K$, but the yield of the hydrogenated products is in this case much lower. Methylcyclohexane is formed from toluene in 8% yield and propylcyclohexane is formed from propylbenzene in 49% yield. In this case, the process is complicated by dealkylation and the reaction products contain methane, cyclohexane, and other compounds.[35]

Evidence for the appreciable reducing activity of LCG with alkali metals is provided by the possibility of using them to synthesise dinuclear carbonyls from metal carbonyls:[36]

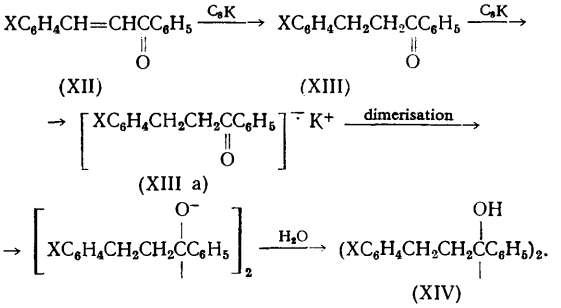
$$2M(CO)_6 + 2C_8K \xrightarrow[25\ ^\circ C,\ 30\ min]{THF} K_2[M_2(CO)_{10}] + 2CO + 16C;$$
$$M = Cr,\ Mo,\ W.$$

Iron pentacarbonyl and dicobalt octacarbonyl can also be reduced with the aid of C_8K to $K_4[Fe_2(CO)_8]$ and $K[Co(CO)_4]$ respectively. The advantages of this reduction procedure compared with methods based on the use of $NaBH_4$ [37] and sodium amalgam[38] is shorter reaction time (30 min against 18–1400 h) and a high selectivity (99%).

LCG with alkali metals are used to reduce a number of ketones.[39] For example, benzophenone is converted quantitatively into benzhydrol (diphenylmethanol) on treatment with C_8K in THF after 2 h at 25 °C. However, the acetophenone reduction process can proceed via two pathways, the corresponding alcohol and pinacol being formed in equal amounts after hydrolysis with water. It has been suggested that the reaction proceeds via the following mechanism:

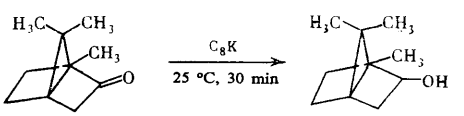


The double bond hydrogenation process and the reduction of the carbonyl group have been described[7] as follows:



On treatment with the LCG with potassium, initially the double bond of the chalcone (XII) is hydrogenated with formation of compound (XIII), which subsequently affords the radical-anion (XIIIa). The dimerisation of the radical-anion (XIIIa) followed by protonation leads to the formation of compound (XIV). The ratio of the yields of compounds (XIII) and (XIV) depends on the nature of the substituent X: the enhancement of its electron-donating character promotes the formation of compound (XIV).

Interesting results have been obtained in the reduction of camphor in the presence of LCG with potassium, whereupon the *exo*-alcohol was detected as the main product:[39]

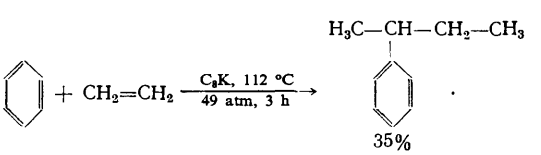


exo (60%)
endo (30%)

If camphor is reduced by traditional methods (using metallic potassium in alcohol or non-intercalated potassium in the presence of graphite), only the *endo*-alcohol is formed. Such regioselectivity of C_8K can be explained by the specific adsorption of the ketone on the surface of the intercalant.

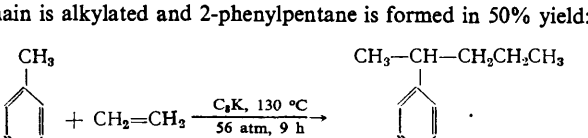
3. Alkylation reactions

One of the first examples of alkylation in the presence of alkali metal intercalants has been the reaction of benzene with ethylene:[40]



The main reaction product is 2-phenylbutane, but other monoalkylbenzenes and *m*-dialkylbenzenes are formed in addition. Under more severe conditions (200 °C, 20 h, 63 atm), the yield of 2-phenylbutane falls to 23% and 19% of biphenyl is formed in addition to the products indicated.

When ethylene interacts with toluene in the presence of C_8K, the side chain is alkylated and 2-phenylpentane is formed in 50% yield:[40]



Under more severe conditions (155 °C, 68 atm, 3 h), the main reaction product becomes n-propylbenzene (48%) and the yield of

2-phenylpentane falls to 17%. It had been shown earlier that alkylation in the side chain can proceed on treatment with metallic sodium but only in the presence of promoting agents (anthracene, phenanthracene, etc.).[41] In this case, mainly n-propylbenzene is formed (57–71%) from toluene and ethylene, while the yield of 2-phenylpentane does not exceed 22%. Thus the C_8K-initiated alkylation is an effective procedure for increasing the length of the side chain in aromatic compounds.

Examples of the alkylation of a series of ketones in the presence of sodium (potassium) on graphite or on wood charcoal have been described.[42] The alkylation of cyclohexanone by methyl iodide, catalysed by sodium on charcoal, affords, together with the monoalkylation (53%) and dialkylation (18%) products, an appreciable amount of cyclohexanol (up to 11%). When sodium in graphite (with hexane as solvent) is used in this reaction, the yield of the reduction product (cyclohexanol) falls to 4% and there is also a simultaneous decrease in the yield of the monosubstitution product (to 40%), while the content of the disubstituted product rises to 27%. If THF is used as the solvent, then the alkylation is complicated still further by reduction (up to 27%) and the yield of the monoalkylated product (23%) becomes almost identical with that of the dialkylated compound (25%). Similar results have been obtained also in the reaction of 2-methylcyclohexanone or 4-t-butylcyclohexane with methyl iodide.[42]

An appreciable yield of the mono-substituted product is achieved in the alkylation of 1- and 2-tetralone with allyl bromide or methyl iodide.[42] For example, in the reaction of 1-tetralone with allyl bromide in hexane in the presence of C_8K, the yield of the monoalkylated product was 98%. A comparable yield (95%) was achieved in the presence of sodium on charcoal. However, when the process was initiated by C_8K in THF, the yield of the monosubstituted compound fell to 62% and the content of the disubstituted product rose at the same time to 38%.[42]

Compounds with an active methylene group, such as nitriles, esters, etc., are capable of being deprotonated in the presence of alkali metal intercalants, forming carbanions which are subsequently alkylated by alkyl halides or react with compounds having a multiple bond, for example with aldehydes. Even a CH acid as weak as acetonitrile is alkylated in THF at a low temperature:[43]

$$RCH_2CN \xrightarrow[4\ h,\ -60\ ^\circ C]{C_8K,\ THF} \left[\begin{matrix}RCHCN^-\\ K^+\end{matrix}\right] \xrightarrow{R^1X} \underset{R^1}{RCHCN} + \underset{R^1}{RCR^1CN}.$$

(XV) (XVI)

R	R^1X	Yield, % (XV)	(XVI)
H	$1\text{-}C_8H_{17}Br$	65	7
H	$C_6H_5CH_2Cl$	42	—
C_6H_5	CH_3I	60	6
C_6H_5	$1\text{-}C_4H_9Br$	67	3

The reaction with esters proceeds similarly:[43]

$$C_6H_5CH_2CO_2C_2H_5 \xrightarrow[4\ h,\ -60\ ^\circ C]{C_8K,\ THF} [C_6H_5CHCO_2C_2H_5]^-K^+ \xrightarrow{RX} C_6H_5CHRCO_2C_2H_5 + C_6H_5C(R)_2CO_2C_2H_5 .$$

(XVII) (XVIII)

RX	Yield, % (XVII)	(XVIII)
CH_3I	70	4
$1\text{-}C_4H_9Br$	70	5
$2\text{-}C_3H_7Br$	45	4

It is noteworthy that mainly monoalkylation occurs in the presence of C_8K, whereas in the reaction employing, for example, t-butyllithium or lithium t-butoxide the yield of the monoalkylated product was 10 and 14% respectively.[44] Thus alkylation in the presence of alkali metal intercalants is a convenient method of synthesis of monosubstituted nitriles and esters.

In the presence of C_8K, nitriles and esters react with aldehydes to form β-hydroxynitriles (XIXa) or β-hydroxy-esters (XIXb) as well as the α,β-unsaturated compounds (XXa) and (XXb); the overall yield of compounds (XIXa) and (XXa) is 35%:[43]

$$C_6H_5CH_2Y \xrightarrow{C_8K} [C_6H_5CHY]^-K^+ \xrightarrow[2)\ H_2O]{1)\ RCHO} \underset{OH}{\overset{Y}{C_6H_5CHCHR}} + C_6H_5CY{=}CHR,$$

(XIXa, b) (XXa, b)

(a) Y = CN; R = C_3H_7, C_6H_5;
(b) Y = $CO_2C_2H_5$; R = C_3H_7, C_6H_5.

On treatment with C_8K, various Schiff bases afford the corresponding aldehydes or ketones:[45]

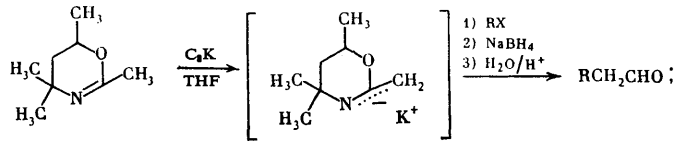
$$RCH_2C{=}NR^1 \xrightarrow[25\ ^\circ C,\ 10\ h]{C_8K,\ THF} \left[\begin{matrix}K^+\\ RCH{\cdots}\overset{\cdots}{C}{\cdots}NR^1\\ R^2\end{matrix}\right] \xrightarrow[2)\ H_2O/H^+,\ 2h]{1)\ R^3X,\ THF} \underset{H}{\overset{R^3}{R-C}}-\underset{R^2}{\overset{}{C}}{=}O;$$

(XXI)

R = H, Alk, Ar; R^1 = t-C_4H_9, cyclo-C_6H_{11}; R^2 = H, Alk; R^3 = Alk; X = Cl, Br, I.

The potassium salt of the enamine anion of type (XXI) is obtained in the first stage. It interacts with alkyl halides and subsequently undergoes acid hydrolysis. The process may be complicated by the Wurtz reaction and it is therefore important to select correctly the reactant ratio in order to obtain the optimum yield of products. Best results (50–70% yield) were obtained for the reactant ratios imine : C_8K : R^3X = 1 : 2 : 2.[45]

The reactions of 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine with propyl iodide and benzyl bromide take place similarly and result in the formation of the corresponding aldehydes in 50 and 58% yields:[45]



R = C_3H_7I, $C_6H_5CH_2Br$.

4. Polymerisation and isomerisation reactions

Alkali metals are known to catalyse polymerisation[46] and it is therefore not surprising that one of the first examples of the use of alkali metal intercalants in organic chemistry was in reactions of this type.

Ethylene polymerises in the presence of catalytic amounts of C_8K in isooctane or n-heptane at 200 °C and 70 atm with formation after 6–20 h of a set of C_8–C_{14} *trans*-monoalkenes and small amounts of solid polyethylene having a low molecular weight and a linear structure.[47] At lower temperatures (120–150 °C) the polymerisation of ethylene does not occur in the presence of the same catalyst even after a period longer than 120 h.

When benzene, toluene, or isopropylbenzene are used as solvents, the compounds are alkylated by ethylene and the yield of polymerisation products falls sharply.[47]

When the polymerisation reactions of ethylene in the presence of metallic potassium sputtered onto potassium chloride and sodium oxide were compared, it was shown that metallic potassium on Na_2O does not initiate this process at all, while in the presence of metallic potassium on KCl the amount of polymerisation product (C_4-C_8) formed is three times smaller than on treatment with C_8K and solid polyethylene is not formed at all. On the other hand, it is known that metallic potassium on Na_2O is an effective catalyst of the interaction of toluene and isopropylbenzene with alkyl halides.[48]

On treatment with C_8K and $C_{24}K$, polystyrene is formed from styrene after 18 h at 30 °C in 17 and 18% yields respectively,[49,50] whereas in the presence of metallic potassium the yield of the polymerisation product reaches 55%. However, in the former case the molecular weight of the polymer is approximately twice as high as in the latter. The yield of the polymer can be increased sharply by carrying out the reaction in solution. Thus the polymerisation of styrene in THF in the presence of C_8K (4 h, 23 °C) affords polystyrene in 98% yield.[51] The most suitable solvent for such polymerisation reactions is THF. The yield of polystyrene was 53% in 1,2-dimethoxyethane, 30% in benzene, and only 5% in heptane. The yield of polystyrene falls also on reducing the potassium content in graphite. Whereas, as stated above, in the presence of C_8K (THF, 4 h, 23 °C) the yield of the polymer reaches 90%, in the presence of $C_{24}K$ it is . . . [part of the Russian text appears to be missing (Ed. of Translation)] under the same conditions, while in the presence of $C_{32}K$ it is only 13%.[51] Methyl methacrylate and acrylonitrile polymerise less effectively than styrene. Thus, when $C_{16}K$ was used as the catalyst, the maximum yield of poly(methyl methacrylate) in THF was 60% and that of polyacrylonitrile was 10%.

Butadiene is polymerised most effectively on treatment with C_8K or $C_{24}K$ in the absence of solvents (30 °C, 30 min), the degree of conversion reaching 100%. In solution (in cyclohexane), the yield of the polymer is usually lower (40–80%).[49]

Isoprene is also polymerised best in the presence of C_8K and $C_{24}K$ without solvent, the yield of the polymer amounting to 100% (12 h, 75 °C, catalyst content 1%).[43] The polymer consists mainly of 3,4-adducts (56 and 44% when C_8K and $C_{24}K$ are used) and *trans*-1,4-adducts (37% in both cases). Polymerisation in cyclohexane (at 75 °C) takes place with a yield of 15–40%. The results of Parrod and Beinert,[50] according to which isoprene polymerises fully in cyclohexane after 12 h at 75 °C and in the presence of the same catalyst, conflict with these data.

The anionic polymerisation of styrene, methyl methacrylate, butadiene, and isoprene is also initiated successfully by the lithium intercalant.[52] Styrene polymerises more effectively in toluene (34.5% after 48 h) than in dimethoxyethane (16.5% after 144 h). The higher activity of lithium fluoride compared with $C_{12}Li$ in the polymerisation of methyl methacrylate is noteworthy: in the presence of LiF in toluene or dimethoxyethane, the degree of reaction of 100%,[53,54] whereas in the presence of $C_{12}Li$ in dimethoxyethane the yield of the polymer is 80% and in toluene it is 0%. The most suitable solvent for the polymerisation of butadiene and isoprene is cyclohexane (15 °C, 42–168 h), the yields of polybutadiene and polyisoprene amounting to 51 and 80% respectively.[52]

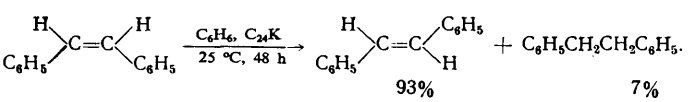
The polymerisation of isoprene on treatment with LCG containing transition metals in potassium results in the formation of a high-molecular-weight amorphous polyisoprene, which consists predominantly of 3,4-adducts.[55] In the presence of graphite compounds containing only a transition metal, isoprene does not polymerise, while the polymer formed on treatment with LCG with potassium contains both 3,4- and 1,4-adducts. The $C_{9.5}CoK_2$ and $C_{9.5}CoK$ catalysts are most stereospecific. In their presence, the content of 3,4-units in polyisoprene reaches 95%. The stereospecificity of compounds having the general formula C_nMK_2 diminishes in the sequence Co > Mo > Fe > Ni. The increase in the potassium content above the stoichiometric value, corresponding to the formula C_nMK_2, reduces the stereospecificity of this reaction.[55]

The polymerisation of epoxyethane takes place successfully on treatment with $C_{24}K$ (THF, 20 °C). For the optimum process time (40–50 min) and catalyst concentration (0.01 M), the degree of polymerisation reaches 60–70%.[56]

The activities of a series of catalysts have been investigated in the polymerisation of β-propiolactone. They can be arranged in the following sequence based on the decrease in activity (the percentage yield of the polymer is indicated in brackets): C_8HgK (100) > $C_{24}K$ (98) > $C_{12}Li$ (94) ≃ $C_{24}K.(DME)_2$ (94) > $C_{28}K.DMSO$ (84) > C_8K (77).[57] $C_{24}K$ in xylene or THF is an effective catalyst of the polymerisation of δ-valerolactone.[58] The yield of poly(δ-valerolactone) in the presence of $C_{24}K$ is 20% smaller than in the presence of metallic potassium (91 and 70% respectively) and exceeds by a factor greater than 2 the yield (44%) attained in the presence of the homogeneous benzophenone/potassium catalyst.[58]

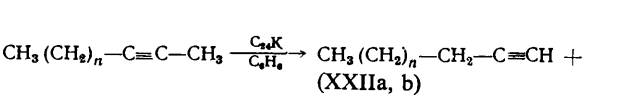
Organocyclosiloxanes polymerise in satisfactory yields (70–80%) in the presence of LCG with potassium or lithium.[59]

On treatment with LCG with alkali metals, unsaturated compounds can be not only hydrogenated but can also undergo the migration of the multiple bond or a change in their steric structure. For example, *cis*-stilbene isomerises wholly to the *trans*-isomer in the presence of $C_{24}K$ under mild conditions:[32]



If this mixture of *cis*- and *trans*-stilbenes is kept at 25 °C for 20 h in the presence of an excess of hydrogen (14 atm), the fraction of the *trans*-isomer rises to 96%.[32]

LCG with potassium initiates the not altogether usual triple bond isomerisation reactions.[33] Thus treatment of dec-2-yne or oct-2-yne with $C_{24}K$ results in the formation of the following products:



	Yield, % (XXII)	(XXIII)
(a) $n=4$ (80 °C, 100 h)	26	2
(b) $n=6$ (25 °C, 48 h)	20	9

These reactions are interesting because of the formation of the terminal 1,2-unsaturated bond, although usually the bond located within the hydrocarbon chain is more stable. Under more severe conditions (80 °C, 60 h), the yield of compound (XXIIb) rises to 65% and, when the reaction is carried out in cyclohexane, the yield of dec-1-yne is 86% (80 °C, 4 h).[32]

5. Condensation and cyclisation reactions

As already stated above, dimerisation processes predominate in the reduction of primary alkyl halides, especially the iodides, in the presence of LCG with alkali metals:[21]

$$C_{18}H_{37}I \xrightarrow[25\ ^\circ C,\ 1\ h]{C_8K,\ THF} C_{18}H_{37}—C_{18}H_{37}.$$

On treatment with C_8K, benzyl chloride and bromide also enter into the Wurtz reaction, affording 1,2-diphenylethane in a high yield.[60] Chlorodiphenylmethane reacts with greater difficulty under these conditions and the dimerisation takes place only to the extent of 50%:[60]

$$(C_6H_5)_2CHCl \xrightarrow{C_8K} \underset{50\%}{(C_6H_5)_2CHCH(C_6H_5)_2}.$$

The product of the reaction of β-chloroethylbenzene in the presence of LCG with potassium is mainly polystyrene (80%) and only 4% of 2,3-diphenylbutane is formed:[60]

$$C_6H_5CH_2CH_2Cl \xrightarrow{-HCl} n\,C_6H_5CH{=}CH_2 \rightarrow -(CH(C_6H_5)-CH_2)_n- \ ; \quad 80\%$$

$$C_6H_5CH_2CH_2Cl \rightarrow CH_3-CH(C_6H_5)-CH(C_6H_5)-CH_3 \ . \quad 4\%$$

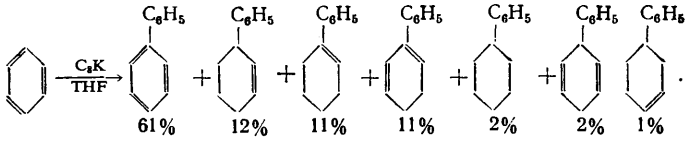
Certain organometallic compounds undergo similar reactions on treatment with LCG with alkali metals. For example, triphenyltin bromide gives rise mainly to hexaphenyl distannate under these conditions:[60]

$$(C_6H_5)_3SnBr \xrightarrow{K/graphite} \underset{53\%}{(C_6H_5)_3Sn—Sn(C_6H_5)_3}.$$

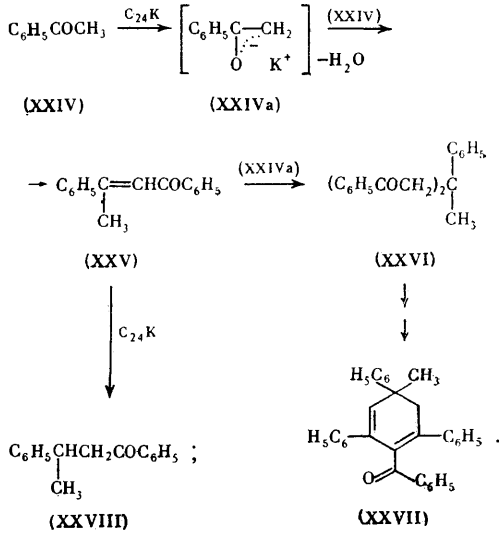
Trialkyl derivatives of chlorosilanes react similarly on treatment with C_8K, affording dimerisation products:[61]

$$R_3SiCl + C_8K \xrightarrow[0^\circ C]{oxolan} R_3Si—SiR_3,$$
$$R = CH_3,\ C_6H_5,\ t\text{-}C_4H_9.$$

It had been noted earlier that benzene is predominantly hydrogenated in the presence of C_8K and H_2 with formation of cyclohexane.[32] In the absence of hydrogen, the reaction in THF proceeds differently:[62]



Under these conditions, quantitative dimerisation, accompanied by partial or complete hydrogenation of one of the rings, takes place. It is of interest to note that the products of the hydrogenation of both benzene rings were not detected. If the process is carried out without THF, no transformation of benzene takes place on treatment with C_8K after four weeks at 50 °C.[62] The condensation of acetophenone can be initiated by various alkali metals (Na and K) and also by $C_{24}K$:[7]



The crotonic condensation of two acetophenone molecules leads to the formation of compound (XXV), which can be hydrogenated with formation of compound (XXVIII) or can enter into the Michael reaction, affording compound (XXVI) as a result of the addition of the enolate anion (XXIVa) to the activated multiple bond. Compound (XXVI) probably also undergoes successive conversion via the Michael reaction and crotonic condensation to the product (XXVII). The ratios of the yields of compounds (XXVI)–(XXVIII) depend on the process conditions. Best results are obtained when metallic sodium is used as the catalyst, whereupon the yield of compound (XXVI) reaches 65–80%. An appreciable amount of the hydrogenated product (XXVIII) (10–15%) is then formed. The yield of the latter compound is reduced if the process is carried out in the presence of $C_{24}K$, but in this case the yield of compound (XXVI) also falls to 45–55%, since compound (XXVI) begins to cyclise to compound (XXVII). The mode of reaction depends significantly on temperature. At 40 °C, 40% of compound (XXVI) and 5% of compound (XXVII) are formed. At 95 °C, only 30% of acetophenone (XXIV) is converted into the product (XXVI), but the yield of compounds (XXV) and (XXVII) increases to 22%. In the presence of a metallic potassium film, the yield of compounds (XXV) and (XXVIII) increases still further, while that of the product (XXVI) falls to 20–40%.

In the presence of LCG with potassium, acetophenone condenses with benzaldehyde, affording a chalcone in a quantitative yield:[63]

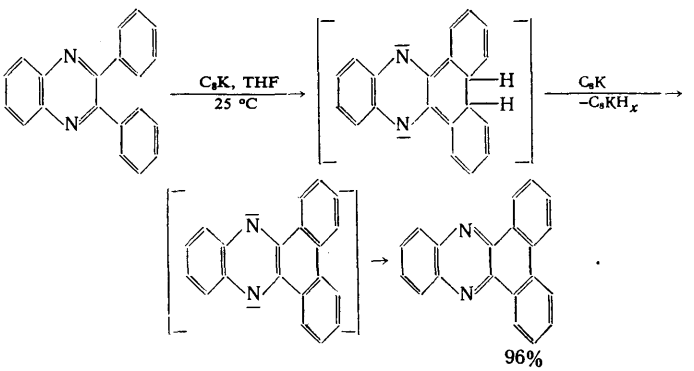
$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 + C_6H_5-\overset{O}{\overset{\|}{C}}H \xrightarrow[-H_2O]{K/graphite} \underset{100\%}{C_6H_5CH{=}CH-\overset{O}{\overset{\|}{C}}-C_6H_5}.$$

Acetone gives rise to the phorone (XXIX) under similar conditions:[63]

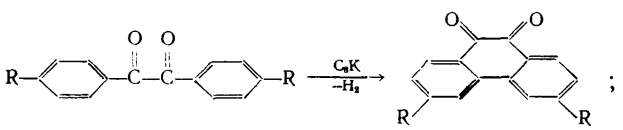
$$3\,CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[-2H_2O]{K/graphite} \underset{(XXIX),\ 86\%}{(CH_3)_2C{=}CH-\overset{O}{\overset{\|}{C}}-CH{=}C(CH_3)_2}.$$

A novel procedure for the intramolecular carbocyclisation of various heterocyclic systems on treatment with C_8K has been described.[64] A series of quinoxalines, namely 2,3-diphenylquinoxaline, 2,3-diphenyldibenzo[*d*]quinoxaline, and 2,3-di-*o*-tolylquinoxaline, give rise to the corresponding phenazines in 60–96%

yields on treatment with LCG with potassium:



The attempts to carry out this reaction in the presence of dispersed potassium (instead of C_8K) lead to the decomposition of the products. DME is preferable to THF as the reaction medium.[64] This method for intramolecular carbocyclisation on treatment with C_8K is fairly general and makes it possible to obtain a wide range of polycyclic compounds. In particular, phenanthrenenequinone can be obtained in this way from benzil in the presence of C_8K:[65]



R=H, CH_3.

6. Other reactions

The sodium intercalant in graphite catalyses the reaction of carbon monoxide with hydrogen (the Fischer–Tropsch reaction),[66] which leads to the formation of a mixture of hydrocarbons ranging from C_1 to C_4:

$$CO + H_2 \xrightarrow[300\ ^\circ C,\ 20\ h]{Na/graphite} \underset{2\%}{CH_4} + \underset{74\%}{(C_2H_6 + CH_2{=}CH_2)} +$$

$$+ \underset{22\%}{(C_3H_8 + CH_2{=}CHCH_3)} + (\text{butane} + \text{but-1-ene}$$

$$+ \textit{cis}\text{-but-2-ene} + \textit{trans}\text{-but-2-ene}).$$

The yield of the products increases if the potassium intercalant in graphite is used together with transition metal chlorides ($FeCl_3$, $RuCl_3$, $OsCl_3$, $MoCl_5$, $PtCl_4$, $NiCl_2$, $PdCl_2$, WCl_6). In the presence of LCG containing only the chlorides (without metallic potassium), this reaction does not occur.

Systems of the type graphite/$FeCl_3$/M (M = K, Na, Rb) catalyse also the synthesis of ammonia from nitrogen and hydrogen:[67]

$$N_2 + 3\,H_2 \xrightarrow[300-350\ ^\circ C,\ 20\ h]{graphite/FeCl_3/M} 2\,NH_3 .$$

M	Yield, %
K	90
Na	52
Pb	43

The catalyst containing potassium is the most active in this process, while that containing rubidium is least active. When $FeCl_3$ in the LCG with potassium is replaced by other salts ($RuCl_3$, $OsCl_3$, $MoCl_5$), the percentage conversion becomes lower and amounts respectively to 30, 60, and 1%. The use of the graphite/$OsCl_3$/K system also leads to the formation of appreciable amounts of hydrocarbons (methane, ethane, etc.).[67]

An interesting application of C_8K has been described.[68] When this intercalant is treated with magnesium iodide, compound (XXX) is obtained. It reacts with a series of alkyl and aryl halides, affording an unusual Grignard reagent (XXXI):

$$2\,C_8K + MgI_2 \xrightarrow[\text{or } C_6H_6]{(C_2H_5)_2O} \underset{\text{(XXX)}}{C_{16}Mg(KI)_2} \xrightarrow{RX}$$

$$\rightarrow \underset{\text{(XXXI)}}{C_{16}(RMgX)(KI)_2} + RMgX,$$

RX = C_2H_5Br, C_6H_5Br, C_6H_5Cl, p-$Br_2C_6H_4$, $CH_3CBr{=}CH_2$.

The reaction takes place more effectively in non-polar benzene (yield 83–98%) than in ether (40–70%). Compound (XXXI), isolated as a friable powder, can be used in classical reactions involving a Grignard reagent (Table 4). It is extremely important that the Grignard reagents obtained in this way can be stored for a long time without a significant loss of their activity.

Table 4. Reactions of $C_{16}(RMgX)(KI)_2$ with electrophiles.[68]

RMgX in $C_{16}(RMgX)(KI)_2$	Electrophile	Yield of product*, %		
		RCOOH	$R(C_6H_5)_2COH$	RH
C_6H_5MgBr	$(C_6H_5)_2CO$	—	88 (84)	—
	CO_2	87 (82)	—	—
	H_2O	—	—	96 (93)
C_2H_5MgBr	$(C_6H_5)_2CO$	—	87 (84)	—
	CO_2	93 (88)	—	—
	H_2O	—	—	95 (92)

* The yields attained using the reagent $C_{16}(RMgX)(KI)_2$ stored for 300 days are indicated in brackets.

The reactions of alkali metal intercalants in graphite with organic perfluoro-compounds (perfluorinated amines, perfluorodecalin, etc.) result in the formation of the corresponding alkali metal fluorides, incorporated in graphite,[69] which are active basic catalysts of certain organic reactions[70] and also function as effective fluorinating agents.[71]

The isotope exchange of hydrogen and deuterium in the presence of LCG with alkali metals has been studied in a number of investigations.[72–74] The activity of the intercalants in this reaction decreases in the sequence $C_{24}K > C_{36}K \gg C_8KH_{0.67} \gg C_8K \simeq 0$. The zero activity of C_8K is evidently due to the fact that neither hydrogen nor deuterium can enter the interlayer space in this inclusion compound owing to the high density of the alkali metal ions.[6] On the other hand, the hydrogen in methane can be exchanged for deuterium in the presence of both $C_{24}K$ and C_8K. The rate of exchange in the presence of $C_{24}K$ is more than twice as high as with participation of C_8K.[75]

The formation of reliably detected radical-anions has been observed[76] in the reactions of $C_{24}K$ with various organic compounds. Examples of the extraction of potassium by a series of organic compounds with formation of the corresponding radical-anions are presented in Table 5. In the case of polycyclic aromatic compounds (Table 5, Nos. 1–7), this process can be described by the following scheme:

$$C_{24}K + x\text{ArH} \xrightarrow{\text{DME}} KC_yDME_z + x[\text{ArH}]^- - K^+DME,\ y>24,\ 1<z<2.$$

The degree of extraction of potassium depends significantly on the electron affinity of the polycyclic compounds. While the degree of extraction of potassium by naphthalene (E_0 = 0.09) is only 18%, that by acenaphthene (E_0 = 1.12) increases to 76%.[76] The appearance of a double bond in the side chain of the arene probably promotes for the same reason an increase in the degree of extraction of potassium (Table 5, cf. Nos. 1 and 9 and 2 and 10).

Table 5. Extraction of potassium from $C_{24}K$ by aromatic compounds[76] (5×10^{-2} M solution in DME, contact time 48 h, 23 °C).

No.	Compound	Electron affinity* (E_0)	Degree of extraction of K, %
1	Biphenyl	0.0	15
2	Naphthalene	0.09	18
3	Phenanthrene	0.17	25
4	Pyrene	0.06	38
5	Coronene	0.70	24
6	Anthracene	0.78	49
7	Acenaphthene	1.12	76
8	α-Methylstyrene	—	11
9	Stilbene	—	18
10	2-Vinylnaphthalene	—	43
11	Benzonitrile	—	75
12	4-Methylbenzophenone	—	80
13	Benzophenone	—	83
14	Fluorenone	—	93
15	1-Cyanopyrene	—	99

* Determined potentiometrically in DME relative to the biphenyl radical-anion.

Aromatic nitriles and ketones (Table 5, Nos. 11–15) are more effective potassium extractants. The formation of radical-anions in such cases probably proceeds in accordance with the following schemes:

$$x\text{Ar}-\text{CO}-\text{Ar} + C_{24}K \xrightarrow{\text{DME}} x[\text{Ar}-\text{CO}-\text{Ar}]^- K^+.\text{DME} + KC_yDME_z,$$

$$x\text{Ar}-\text{CN} + C_{24}K \xrightarrow{\text{DME}} x[\text{Ar}-\text{CN}]^- K^+.\text{DME} + KC_yDME_z.$$

The examples presented demonstrate the high electron-donating capacity of LCG with alkali metals in relation to weak electron acceptors and confirm the hypothesis that the layers of graphite in LCG with alkali metals can be regarded as macropolyanions in which electrons are located in different energy levels.

* * *

Thus layered compounds of graphite with alkali metals are used in various fields of organic synthesis as Lewis bases and one-electron reductants. Their advantages over alkali metals consist in the fact that they ensure milder reaction conditions and easier separation of the reaction products and make it possible to regulate the selectivity and stereoselectivity of the processes by varying the nature of the alkali metal in the LCG and the type of intercalant. The high sensitivity of LCG with alkali metals to the presence of traces of oxygen and water should be included among the disadvantages of their use in organosynthesis.

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Introduction of a carbon–carbon bond into electron-deficient aromatic compounds

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ABSTRACT. Methods for introducing a new carbon–carbon bond into aromatic compounds containing such electron-accepting groups as NO_2, SO_2CF_3, or oxazoline and into perfluoroarenes are discussed in the review. These methods comprise S_NAr reactions, oxidation of anionic σ-complexes, isolated previously or obtained *in situ*, and vicarious nucleophilic substitution reactions.

The bibliography contains 371 references.

Contents

I. Introduction 750
II. Nucleophilic aromatic substitution reactions 750
III. Preparation of anionic σ-complexes containing C=C bonds and their oxidation 757
IV. Alkylation of mononitro aromatic compounds 765

I. Introduction

The interest of organic chemists in nucleophilic aromatic substitution, and in anionic σ-complexes as possible intermediates in these reactions, has not weakened during almost four decades. Both the overall number of publications and the continuous appearance of new reviews and monographs indicate this.[1–20] In spite of apparent outward simplicity the nucleophilic aromatic substitution reaction is distinguished by the complexity and diversity of its mechanisms.

Reactions of the S_NAr type which lead to the formation of a new C–C bond have special significance and are consequently extremely important in organic synthesis. Such reactions occur most smoothly with perfluoroarenes. However for several halonitroarenes they proceed in a far more complex manner and frequently lead to mixtures of products. The functionalisation of nitroarenes has great importance since the compounds obtained serve as starting materials for the synthesis of various biologically active heterocycles.[21,22]

It is well known that at first a rapid and reversible formation of anionic σ-complexes occurs at an unsubstituted carbon atom in the reaction of charged nucleophiles with electron-deficient arenes. The most stable of these are complexes with carbon–carbon bonds since their rearrangement into 1,1-σ-complexes, from which substitution products are then formed, proceeds most slowly. As a result they are able to undergo various conversions such as entering into oxidation-reduction reactions with the participation of the nitro group. These complexes may also be oxidised by suitable oxidising agents so that halogens and other substituents in the benzene ring are unaffected. Thus the preparation of anionic σ-complexes and their subsequent oxidation may be an alternative method of introducing a C–C bond into an electron-deficient arene. It is probable that this very route is the most acceptable for substrates containing several electron-accepting groups such as 1,3,5-trinitrobenzene or 1,3,5-*tris*-(trifluoromethylsulphonyl)benzene which form stable σ-complexes. However good results were also obtained when oxidising unstable σ-complexes formed from mononitroarenes.

Arenes activated by an oxazoline group, besides nitro- and *tris*-(trifluoromethylsulphonyl)-aromatic compounds, are widely used at present as substrates in S_NAr type reactions. Although the activating effect of this group is weaker than that of a NO_2 group similar compounds prove to be valuable intermediates in synthesis.

Methods are discussed in the present review for introducing a C–C bond into electron-deficient arenes and include nucleophilic substitution of halogen and hydrogen. Since there are practically no data on reactions of the S_NAr type with carbanions in the known reviews[1–5] and monograph[6] they are considered in ample detail in the present review. On the other hand a whole series of reviews[7–19] and a recently published fundamental monograph[20] have been devoted to anionic σ-complexes and contain information on complexes with various types of C–Nu bonds, and on their physicochemical characteristics and stability constants. Consequently we will not list all the σ-complexes with C–C bonds obtained to date in the present review but will indicate only the main carbanions with which σ-complexes are successfully obtained. Principal attention will be paid to the conditions for obtaining σ-complexes and also to the methods for aromatising them.

Reactions for adding organometallic compounds and carbanions to mononitroarenes are segregated into a separate section. Removal of hydride ion from an intermediate unstable σ-complex occurs only under the action of an external oxidising agent or a nitroarene. The interesting vicarious nucleophilic substitution reactions are included here.

The limited size of the review does not permit inclusion of S_NAr type reactions (and the formation of σ-complexes) in neutral and cationic complexes of arenes with the transition metals, which are being widely studied at present. Reactions with carbanions in the heterocyclic series have been partially considered in reviews which have appeared comparatively recently.[23,24]

II. Nucleophilic aromatic substitution reactions

1. Substrates activated by NO_2, SO_2CF_3 and oxazoline groups

a) Substitution of halogen

As mentioned above halonitro derivatives are the most frequently used subjects of nucleophilic aromatic substitution reactions since the nitro group is one of the very strong electron-accepting substituents

Table 1. Replacement of halogen in halonitrobenzenes by carbanions of malonic, acetoacetic and cyanoacetic esters and of acetylacetone.

No.	Substrate	Carbanion from	Group replaced	Solvent	Yield, %	Refs.
1	1-Chloro-2-nitrobenzene	$NaCH(COOEt)_2$	Cl	t-BuOH	54	[32]
2	1-Bromo-2-nitrobenzene	$NaCH(COOEt)_2$	Br	Et_2O		[31]
3	4-Bromo-3-nitrobenzonitrile	$NaCH(COOEt)_2$	Br	Et_2O		[31]
4	1,3-Dichloro-2-nitrobenzene	$NaCH(COOEt)_2$	Cl	t-BuOH	84	[32]
5	1-Chloro-2,4-dinitrobenzene	$NaCH(COOEt)_2$	Cl	EtOH		[30]
6	1-Bromo-2,4-dinitrobenzene	$NaCH(COOEt)_2$	Br	EtOH		[33, 35]
7	1-Chloro-2,6-dinitrobenzene	$NaCH(COOEt)_2$	Cl	Et_2O		[25]
8	1-Chloro-4-methyl-2,6-dinitrobenzene	$NaCH(COOEt)_2$	Cl	Et_2O		[27]
9	1,5-dichloro-2,4-dinitrobenzene	$NaCH(COOEt)_2$	Cl	Et_2O		[28]
10	1-Chloro-2,4,6-trinitrobenzene	$NaCH(COOEt)_2$	Cl	$EtOH+C_6H_6$		[29]
11	1-Chloro-2,4-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	75	[37]
		NaCH(COOEt)COMe	Cl	Et_2O	74	[45]
		NaCH(COOEt)COMe	Cl	EtOH		[30, 36]
12	1-Chloro-2,6-dinitrobenzene	NaCH(COOEt)COMe	Cl	EtOH	90	[26]
13	1,2-Dichloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	59	[41]
14	1-Bromo-2-chloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	88	[38]
15	1-Chloro-2-iodo-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	57,4	[40]
16	1,4-Dichloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	56	[42]
17	1-Bromo-4-chloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	98	[39]
18	1-Chloro-4-iodo-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	84	[43]
19	1,5-dichloro-2,4-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	80	[30]
20	1-Chloro-2,4,6-trinitrobenzene	NaCH(COOEt)COMe	Cl	EtOH		[44]
21	1-Chloro-2-nitrobenzene	NaCH(CN)COOEt	Cl	t-BuOH	70	[43]
22	1-Chloro-4-nitrobenzene	NaCH(CN)COOEt	Cl	EtOH		[46]
23	1-Chloro-2,4-dinitrobenzene	NaCH(CN)COOEt	Cl	EtOH	90	[46]
24	2-Chloro-5-nitrobenzonitrile	NaCH(CN)COOEt	Cl	EtOH		[30]
25	1-Chloro-2,4,6-trinitrobenzene	NaCH(CN)COOEt	Cl	EtOH	53	[46]
26	1-Chloro-2,4-dinitrobenzene	$NaCH(COMe)_2$	Cl	EtOH	54	[47, 48]

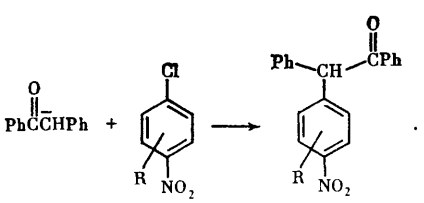
and halogen is a good leaving group. The activating influence of other electron-accepting groups (CN, CF_3, COR, etc.) for substitution of halogen in ArX usually proves to be insufficient.

The substitution of halogen under the action of anions of malonic,[25–33] acetoacetic[26,30,34–35] and cyanoacetic[30,43,46] esters and acetylacetone[47,48] in ether and alcohol has been studied recently. In these solvents carbanions display fairly low reactivity, they react successfully with strongly activated di- and trinitrohalobenzenes where yields are satisfactorily high (Table 1).

For example the sodium salts of malonic and acetoacetic esters do not react in alcohol with 2-chloro-5-nitrobenzonitrile† or with 2-chloro-5-nitrobenzoic acid.[30] However in t-butanol the potassium salts of cyanoacetic and malonic esters react successfully with *o*-chloronitrobenzene and give low yields of substitution products in ether and ethanol.[32] Generally speaking these studies are fairly complex to analyse since product yields are often not given. It is interesting to mention that the structures of the α-picryl and 2,4-dinitrophenyl derivatives of acetoacetic ester, obtained at the end of the past century,[44] were established only comparatively recently. It was shown that they were enols not only in solution[45,49,50] but also in the solid state.[51] α-Picrylacetylacetone is completely enolised in solution.[52]

The new stage in the study of nucleophilic aromatic substitution is linked with the use of dipolar aprotic solvents of the type of dimethylsulphoxide (DMSO), hexamethylphosphoramide (HMPA) or pyridine (Py) which usually smooth the course of the reaction. Thus the sodium salts of malonic ester and acetylacetone react with *o*-chloronitrobenzene, *p*-chloronitrobenzene, and 1,4-dichloro-2-nitrobenzene in dimethylformamide (DMF), DMSO and HMPA at 100 °C in 1 to 5 h, the yields of arylation products being from 20 to 65%.[53] Arylation of phenylacetonitrile with *p*-chloronitrobenzene was carried out successfully in pyridine in the presence of KOH.[54]

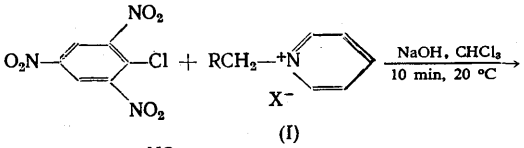
Arylation of the carbanion of desoxybenzoin by various halonitrobenzenes was carried out in DMSO and DMF, *p*-halonitrobenzenes gave products in ~60% yield but *ortho* isomers reacted non-selectively and yields of substitution products were low.[55]



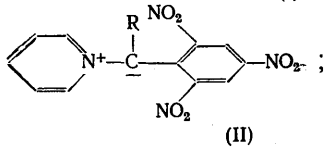
In aromatic nitrotoluenes the methyl group located in the *para* position to the nitro group may be deprotonated under the action of base. It was shown that 2,4,6-trinitrotoluene reacts in the presence of MeONa with picryl chloride, 1-chloro-2,4-dinitrobenzene, 1-fluoro-2,4-dinitrobenzene and 1,3-dibromo-2,4,6-trinitrobenzene with the formation of polynitrodiphenylmethanes.[56] Highest yields of products were achieved on carrying out the reaction in a tetrahydrofuran (THF)–DMSO mixture however even under these conditions 2,4,6-trinitrotoluene did not react with mononitro- and 1-halo-3,5-dinitro- and 1-halo-2,6-dinitrobenzenes.[56]

†A report on the isolation of a product from the reaction of sodiomalonic ester with 4-bromo-3-nitrobenzonitrile is seemingly erroneous.[32,30]

Among the other reactions of halonitrobenzenes with carbanions it is necessary to mention the preparation of ylids (II) by reacting picryl chloride with quaternary salts of pyridine (I) in the presence of alkali.[57]



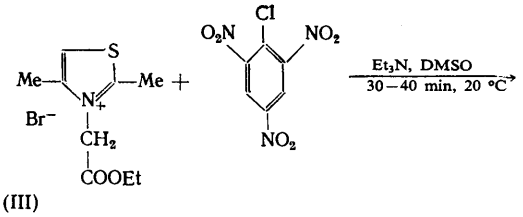
(I)



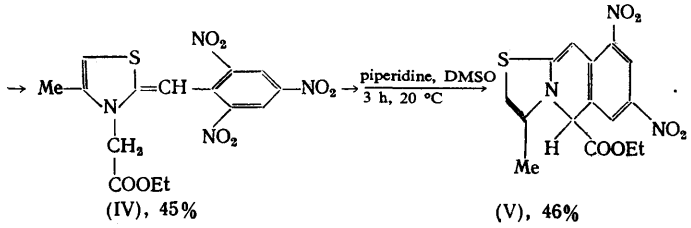
(II)

R = PhCO, MeCO etc.

Reactions of picryl chloride with salts of type (III) in DMSO in the presence of base lead to the formation either of ylid (IV) or the product of intramolecular substitution (V) of a nitro group by the carbanion of ylid (IV).[58]

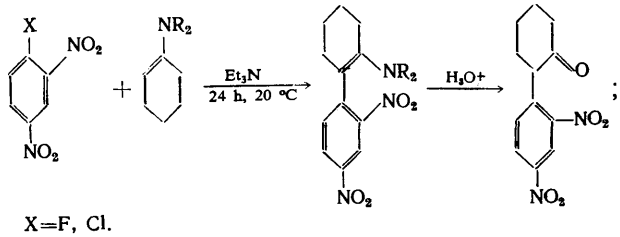


(III)



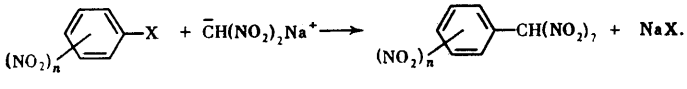
(IV), 45% (V), 46%

Products of substitution of the halogen atom in 1-chloro-2,4-dinitrobenzene or 1-fluoro-2,4-dinitrobenzene by enamines were obtained in 80–90% yield in the presence of an equimolar quantity of triethylamine.[59] It was noted that in the absence of Et_3N yields were sharply reduced (to 6–30%).



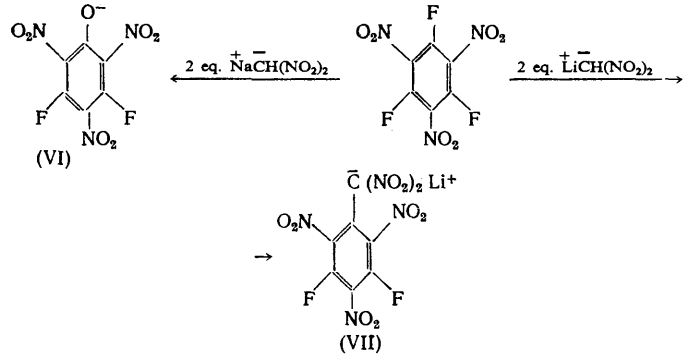
X=F, Cl.

Reactions of the sodium salt of dinitromethane with various halonitrobenzenes in DMF have been investigated.[60]



1-Halo-2,4-dinitrobenzenes displayed the greatest reactivity in this reaction. The reaction of 1,2-dichloro-4-nitrobenzene and 1,4-dichloro-3-nitrobenzene with $\bar{C}H(NO_2)_2Na^+$ was not complete even after a year (20 to 25 °C); *o*- and *p*-chloronitrobenzenes and 2,3,5,6-tetrachloro-3-nitrobenzene generally did not react.

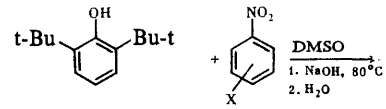
2,4-Dinitrophenoxide and picrate were isolated on attempting to react the sodium salts of bromodinitromethane and trinitromethane with 1-chloro-2,4-dinitro- and 1-chloro-2,4,6-trinitrobenzenes respectively.[60] The picrate (VI) was isolated from the reaction of 1,3,5-trifluorotrinitrobenzene with the Na salt of dinitromethane. However use of the Li salt made it possible to obtain the *C*-arylated product (VII) in 43% yield[61] (see also p. 755). Regrettably no opinion was expressed on possible routes of forming phenoxides and picrates.[60]

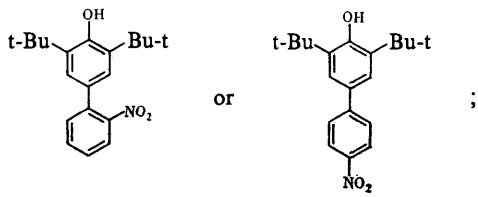


(VI)

(VII)

Phenoxide ions and aromatic amines occasionally emerge as *C*-nucleophiles in S_NAr type reactions[62–66] (see also p. 761). Usually 2,6-dialkylphenols react with *p*-chloronitrobenzene in DMSO in the presence of KOH giving diphenyl ethers.[62] However 2,6-di-(t-butyl)phenol forms *C*-arylation products under these conditions[62,63] (cf. p. 761).

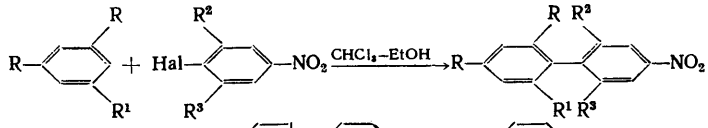




64–97%

X = 2-F, Cl, Br, I, NO_2, SO_2Ph, 4-NO_2.

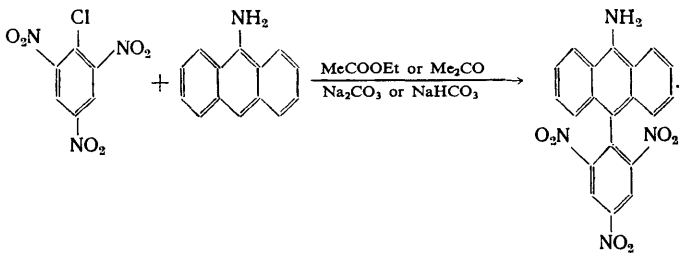
Diaryls formed by reaction of aminobenzenes with activated aryl halides are intensely coloured and are intramolecular charge-transfer complexes.[65,66]



R, R^1 = N⟨ , N⟨ , NMe_2, N⟨ O;

Hal = F, Cl; R^2, R^3 = NO_2, H, CN, CO_2Me.

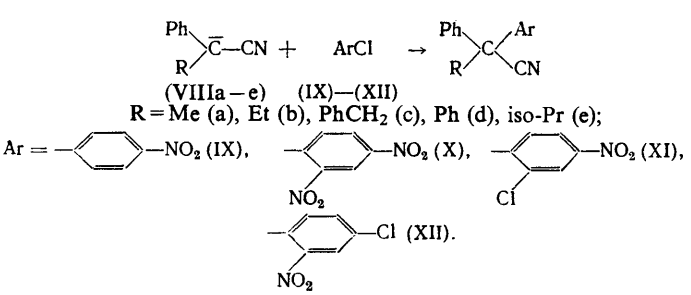
The reactivity of ArHal and arylamines in these reactions varies within wide limits. Thus the interaction of picryl chloride, the most reactive of all the aryl chlorides, with all triaminobenzenes proceeds readily, with dipyrrolidino- and dipiperidinobenzenes more extended heating is required and with mono(dialkylamino)benzenes generally does not occur.[65] Products of *C*-arylation were also obtained in the reaction of 9-aminoanthracene and 2-amino-*N*-methylindole with picryl chloride.[66]



It was noted that the remaining primary amines investigated (derivatives of benzene, diphenyl, naphthalene, pyridine, quinoline, carbazole, etc.) were arylated at nitrogen.[66]

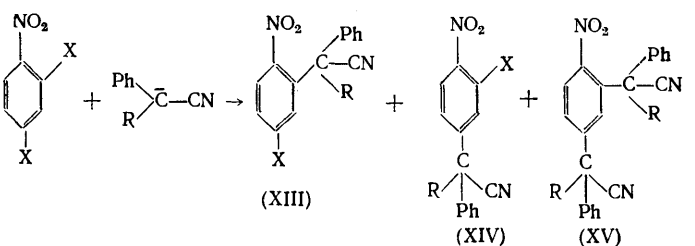
The application of dipolar aprotic solvents has therefore extended significantly the scope of the nucleophilic aromatic substitution reaction, however the high cost of these solvents and mainly the difficulties of separating the reaction products from them significantly limit their use. The application of phase-transfer catalysis (PTC) is more promising.[67–69] Good results were obtained on using PTC to prepare polynitrodiphenylmethanes from 2,4,6-trinitrotoluene and picryl chloride or 1-chloro-2,4-dinitrobenzene. Reaction was effected in methylene chloride in the presence of aqueous alkali solution and a phase transfer agent (18-crown-6 ether, $PhCH_2\overset{+}{N}Et_3Cl^-$), yields of products were ~90%.[70]

The PTC method has been successfully applied for the arylation of alkyl- and phenylacetonitriles with various chloronitrobenzenes in a system of 50% aqueous NaOH in the presence of triethylbenzylammonium chloride. Yields of products were 80–90%.[54,71–75]



Regrettably not all reactions proceed readily under these conditions. For example, in the case of carbanions (VIIId) and (VIIIe) the results varied with the nature of ArCl and the reaction conditions. Both carbanions form normal substitution products with chlorodinitrobenzene (X) however nitroarylation occurs only in the presence of DMSO with 1,2-dichloro-3-nitrobenzene (XI). In the absence of DMSO (VIIId) and (XI) react to form 1,1-dicyanotetraphenylethane and reduction products of the nitro group but 4-chloro-2-nitrophenol is formed from (VIIIe) and (XII) in the presence of DMSO.[54]

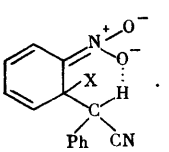
It was also noted that anions of active methylene compounds (phenylacetonitrile, desoxybenzoin, ethyl cyanoacetate, malonic ester) do not form arylation products under PTC conditions in good yield.[55,74,75] These reactions are successfully effected in aprotic dipolar solvents.[53–55] It is interesting that such carbanions replace the halogen in the *ortho* position of 2,4-dihalonitrobenzenes although the yield of product (XIII) was fairly low.[75] These reactions always give a complex mixture of products and are accompanied by resinification to a significant extent (see also pp. 768 and 769). However carbanions of phenylalkylacetonitriles and also ethyl malonate replace halogen predominantly at the *para* position.[75]



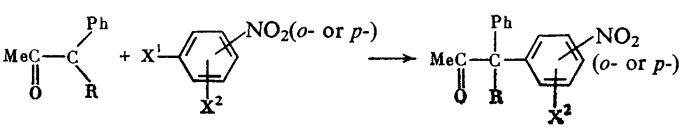
X = Cl, Br; R = Me, $PhCH_2$, Et, Ph, H.

The yield of product (XIV) was 70–90%, compounds (XIII) and (XV) if formed were in minimal amounts (2–4%). Compounds (XIII) and (XV) were obtained in somewhat larger yield from benzylphenylacetonitrile (15.6% and 10.7% respectively).

The observed phenomenon of the preferential replacement of the *ortho* halogen in 2,4-dihalonitrobenzenes is explained by the *ortho* effect of the nitro group which is also known for reactions with other nucleophiles. In the reaction of 1,3-dihalo-4-nitrobenzenes with tertiary amines and anionic reagents, the halogen atom in the *para* position is the more reactive while with primary and secondary amines the *ortho* halogen is more reactive.[3] It was suggested that the presence of hydrogen atoms in the anion enables the formation of an intramolecular hydrogen bond with the *ortho*-nitro group in the σ-anionic complex which leads to its further stabilisation and increases the rate of nucleophilic substitution of the halogen atom in the *ortho* position (see also Chapter IV, section 2).



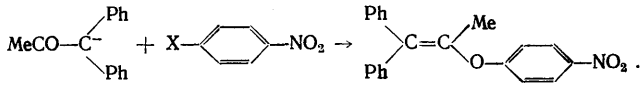
Nitroarylation of ketone enolates has been carried out in aprotic dipolar solvents and in a two-phase catalytic system.[76]



R=H, Et, Pr, Bu; X^1=F, Cl; X^2=H, Cl, NO_2.

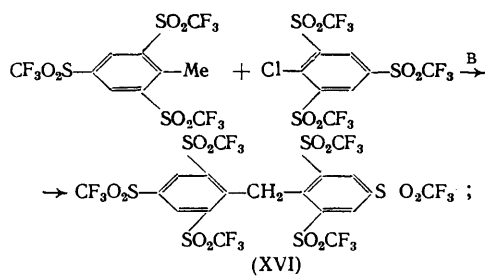
The reaction of benzylmethylacetone with halonitrobenzenes has been carried out in DMSO or DMF using NaOH or NaH. 1-Alkyl-1-phenylacetones are arylated better in a two-phase system, the reaction being accelerated by small additions of DMSO. Yields

were higher for *o*- and *p*-fluoronitrobenzenes than for the chloro derivatives. It was noted that only the product of *O*-arylation was isolated on arylation of 1,1-diphenylacetone under these conditions.[76]



It is evident from the material stated above that carrying out a nucleophilic substitution reaction under PTC conditions is promising. Regrettably it was impossible to react the most reactive nitroaromatic compounds of the picryl halide type with insufficiently stable carbanions under these conditions.

It is known that the SO_2CF_3 group displays an even stronger electron-accepting effect than the nitro group. Like 2,4,6-trinitrotoluene 1-methyl-2,4,6-*tris*-(trifluoromethylsulphonyl)benzene reacts readily in the presence of various bases (B) with 1-chloro-2,4,6-*tris*-(trifluoromethylsulphonyl)benzene with the formation of the corresponding diphenylmethane (XVI).[77]

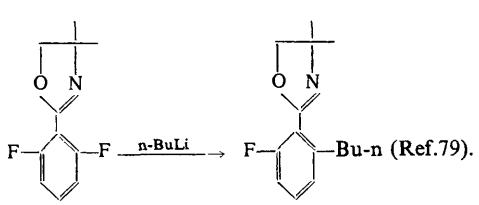


(XVI)

B = MeMgI (yield 16–57%), NaH (17%), KOH (47%), KF (79%).

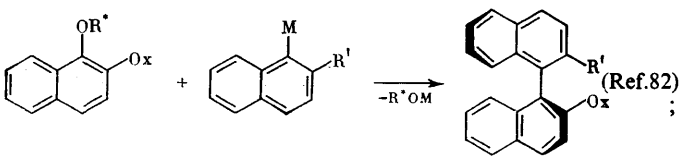
In this case KF proved to be the most effective base.

Several papers have appeared very recently in which the activating influence of the oxazoline group in nucleophilic aromatic substitution reactions has been reported.[78–86] This group is valuable because nucleophilic substitution reactions of various organomagnesium and organolithium compounds occur readily in its presence and the oxazoline group itself may be converted into carboxyl, ester or amide.[78] A fluoride or methoxyl group in the *ortho* position to the oxazoline ring may emerge as leaving group.[78]

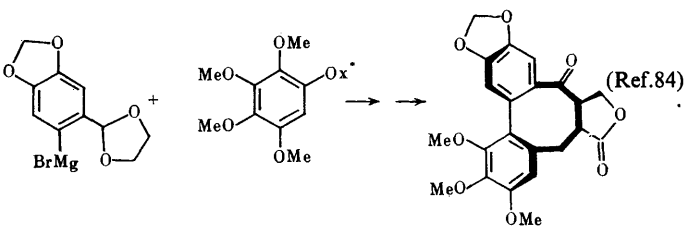


The introduction of the oxazoline group to activate the aromatic nucleus has enabled the development of methods of obtaining chiral biaryls. Good results were obtained both on using a chiral leaving group OR* and a chiral oxazoline fragment OX*.[81–84] However it is necessary to note that the activating influence of the oxazoline group frequently proved to be insufficient to effect a nucleophilic substitution with stabilised carbanions.

Several studies on the kinetics of the reaction of halonitrobenzenes with carbanions are known.[52,87–96] In all cases the nucleophilic substitution reaction is considered as a two-step process where the rate-determining step is the formation of a 1,1-σ-complex and the removal of halide ion occurs in the subsequent rapid step‡. This is the most common situation for an S_NAr mechanism.[52,87–90]

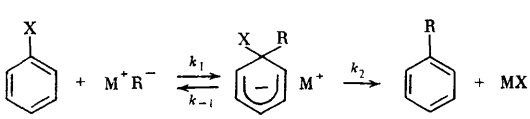


(Ref.82);



(Ref.84).

It should be noted that on the basis of purely kinetic data is is probably impossible in these cases to establish the rate-determining step although indirect data indicate that such a mechanism is correct.[52,87,89] From general considerations it is also evident that the halide removal step (k_2) must not be slower than breakdown of the carbanion (k_{-1}).



This was confirmed by data on the influence of the nature of the leaving group on the rate of halogen replacement in the reactions of *p*-halonitrobenzenes with fluorenyl anions.[91] It was shown that the reaction rate increases in the series F > Cl > Br > I. Results on a study of competing substitution of halogen atom in dihalonitro compounds under the action of anions of malonic and acetoacetic esters are in agreement with this conclusion (see also Table 1).[38–40,43] Similarly for chloropentafluorobenzene reacting with 9-carbomethoxyfluorenyl anion where preferential replacement of the fluoride ion in the *para* position to chlorine was observed.[92,93] Essentially the formation of a 1,1,-σ-complex has not been established in any of the work in which the kinetics of halogen replacement have been studied. It is known that picryl chloride and even 1-halo-2,4-dinitrobenzene form stable 1,3-σ-complexes in reactions with nucleophiles, including carbanions, and these complexes have been isolated and characterised by PMR spectroscopy.[97–99] These complexes are sometimes very stable, as for example in the case of R = CH_2COMe which gave no further substitution product or this conversion occurs very slowly. The 1,3-σ-complexes formed on interacting picryl chloride with anions of malonic and cyanoacetic esters[52,88,89] or malondinitrile[90] are seemingly less stable (lower pK_a values for the CH-acid) and subsequently rearrange into 1,1-σ-complexes (not recorded) which also give substitution products.

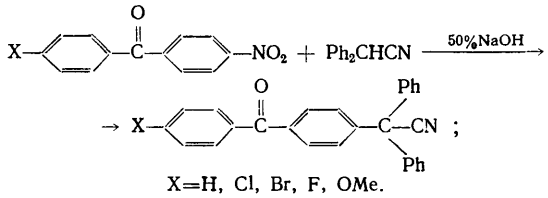
‡The rate-determining removal of halide ion has been proposed.[95,96] However the conclusions were incorrect since these authors proceeded from the false premise of assuming the 1,1-σ-complex to be more stable than the 1,3-σ-complex.

When the group being replaced is MeO^- the second step may remain slow. Such a situation was observed in the reaction of 2,4,6-trinitroanisole with anions of malonic and cyanoacetic esters.[100,101]

It was noted above that high yields of halogen substitution products were successfully achieved on carrying out the reaction in DMSO or under PTC conditions, i.e. in systems where carbanions are in the form of free ions or solvent-separated ion pairs. On the other hand in systems of NaH (or $NaNH_2$)–ether (or THF, benzene) yields of products were, as a rule, low.[54] In these solvents carbanions usually form contact ion pairs or associates. Similar rules for the influence of the medium or of the counter-ion were confirmed by results on the study of the kinetics of arylation of the Na salts of cyanoacetamides and of the K salts of 9-carbomethoxyfluorene by halonitrobenzenes. Here the free ions react at a greater rate than the ion pairs.[92,93,102] The exception was the arylation reaction of the Na salt of *N,N*-dimethylcyanoacetamide by *o*-chloronitrobenzene where the ion pair proved to be more reactive than the free ion. The authors linked this with stabilisation of the σ-anionic complex formed by coordination of the counter ion with oxygen of the nitro group.[102]

b) Replacement of other groups

It is known in principle that the nitro group is a fairly good leaving group under conditions when it is activated by another electron-accepting substituent.[4] Examples of such substitution under the action of carbanions are sparse as yet. The substitution of a nitro group in nitrobenzophenones occurs readily under PTC conditions.[54]

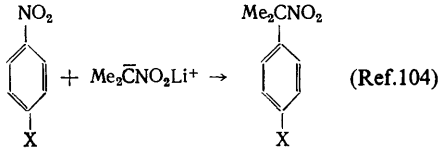


X=H, Cl, Br, F, OMe.

Replacement of a nitro group also takes place in the reaction of perfluoronitrobenzene with perfluoro-t-butyl anion.[103]

$$C_6F_5NO_2 + (CF_3)_3C^- \rightarrow C_6F_5C(CF_3)_3.$$

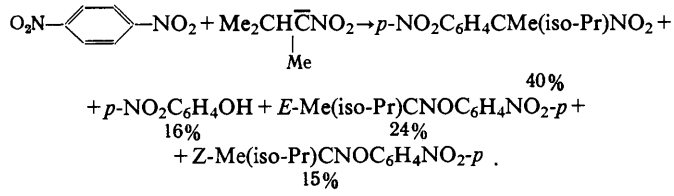
Anions of nitroalkanes (Li salts of 2-nitropropane, 2-nitrobutane[104] and 2-R-5-nitro-1,3-dioxan[105,106]) were used in the majority of studies on nitro group substitutions.

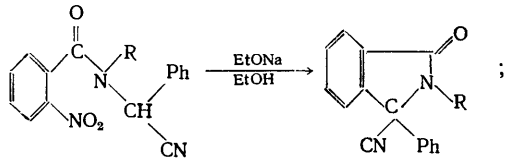


X = NO_2, CN, SO_2Ph, COOMe, COPh.

It was noted that tetrabutylammonium salts of nitroalkanes are more reactive than Li salts.[107,108] For example the reaction of *p*-dinitrobenzene (*p*-DNB) with tetrabutylammonium salts in DMSO, benzene and acetone was complete in less than 5 min while with Li salts only after 3 to 30 h.[107]

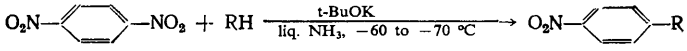
The reaction of *p*-DNB with 1,2-dimethyl-1-nitropropane anion in benzene and in DMSO occurs in a more complex manner. In addition to the normal substitution product *p*-nitrophenol and *p*-nitrophenyl ethers of methylisopropylketoxime were formed.[107,108]





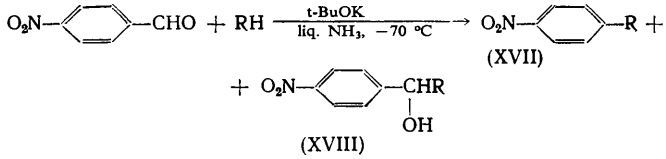
R = Me, $PhCH_2$.

The reacting carbanions may be obtained *in situ* from the corresponding CH-acids in the presence of t-BuOK as was shown for the reaction of *p*-DNB with various RH in liquid NH_3.[110]



R = CH_2COMe, CH(Me)COEt, CH_2COOEt, CH_2CN, CH(Ph)CN etc.

In the case of *p*-nitrobenzaldehyde an unusual substitution was observed under these conditions when fission of a carbon-carbon bond occurred.[111]



(XVII)

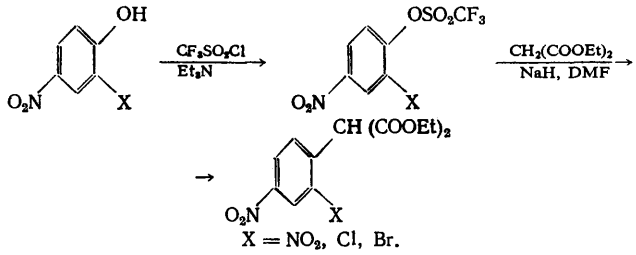
(XVIII)

R = CH_2COOMe, CH_2COBu-t, CH_2COOEt, CH(CN)Ph etc.

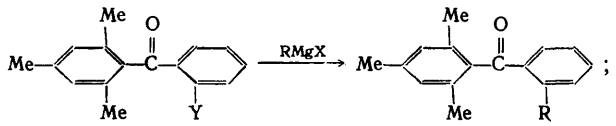
The reaction of *p*-nitrobenzaldehyde with t-BuCOMe was carried out in the presence of various bases. It turned out that systems of t-BuOK/liq.NH_3 and KNH_2/liq.NH_3 were the most effective, yields of substitution products (XVII) were 64% and 71% respectively. The use of other systems, and particularly t-BuOK/t-$BuNH_2$, t-BuOK/THF, t-BuOK/ether, t-BuOK/DMF, $NaNH_2$/liq.NH_3 led to a lower yield of product (XVII). On using the n-BuLi/THF system only alcohol (XVIII), R = CH_2CO-t-Bu was obtained in 76% yield. The reaction mechanism is unknown. Strictly speaking the mechanism has not been established and it is possible, for the nitro group substitution reactions enumerated above, that an $S_{RN}1$ mechanism is effected in some of them.

One of the best leaving groups in reactions of the S_NAr type is the triflate group which is replaced more readily than a nitro group. The example given below illustrates the possibility of applying the

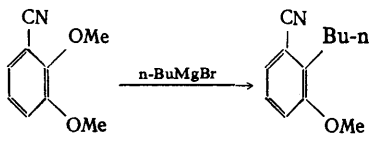
reaction to the synthesis of nitroarylmalonic esters (and nitroarylacetic acids and oxindoles in general) from the corresponding phenols.[112]



There is also information on other groups. For example methylphenylketones, having a leaving group Y in the *ortho* position, react with RMgX with the formation of products of the aromatic substitution of Y.[113–115]



Replacement of the OR group under the action of a Grignard reagent has been shown.[116–118]

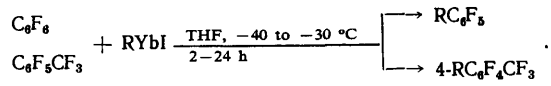


The majority of the carbanions considered in S_NAr reactions are ambident which raises the question of possible arylation at two centres. It is noted that the nature of the leaving group is one of the principal factors controlling the direction of *C*- and *O*-arylation of alkali metal salts of carbonyl compounds. For example the quantity of *C*-isomer falls along the series OPh < Hal < OMe < OAc < OSO_2Me in the reaction of picryl chloride with enolates of β-dicarbonyl compounds with an increase in the hardness of the leaving group. The structure of the enolate, the nature of the alkali metal and the solvent also influence the course of the reaction in a substantial manner. Other conditions being equal the use of softer enolate ions, cations of a lower radius and less polar aprotic solvents aid the preference for *C*-isomer formation.[119–122]

2. Nucleophilic substitution reactions in perfluoroarenes

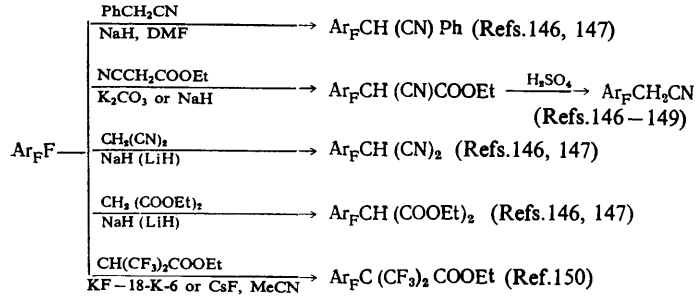
As already mentioned in the Introduction perfluoroarenes react fairly readily by the S_NAr type reaction both with organolithium and with organomagnesium compounds and with carbanions. Aryl (Ph, 3,5-dibromopyridyl, thienyl) and alkyl (Me, Bu) groups have been introduced into the perfluoroaromatic ring by the action of RMgX or RLi.[123–141] Yields of substitution products were fairly high (up to 70%) in several cases, however the reactivity of organomagnesium compounds occasionally proved to be inadequate and the more reactive lithium derivatives led to the formation of disubstitution byproducts. Even in the case of the less reactive propenyl and acetylenyl lithium derivatives a mixture of mono- and disubstituted products was formed as a rule.[138–141]

It was shown comparatively recently that organoytterbium compounds are excellent nucleophilic reagents in substitution reactions at vinyl and aromatic carbon atoms.



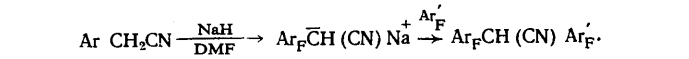
A comparative study of nucleophilic substitution reactions of perfluoroarenes under the action of RYbI, RLi and RMgX (R = Ph, Bu, PhC≡C) showed that RYbI (R = Ph, Bu) surpassed RLi in selectivity of substitution and the more preferred RMgX in the yield of desired products. However of the phenylacetylenyl derivatives only PhC≡CLi was capable of replacing fluoride ion in reactions with C_6F_6 or $C_6F_5CF_3$.[144] It is noted that iodine in pentafluoroiodobenzene is replaced by the action of copper phenylacetylide.[145]

Various carbanions, generated *in situ* from CH-acids using NaH, LiH, K_2CO_3 (usually in DMF), KF or CsF as bases, are involved in nucleophilic substitution reactions with perfluoroaromatic compounds.[146–150]

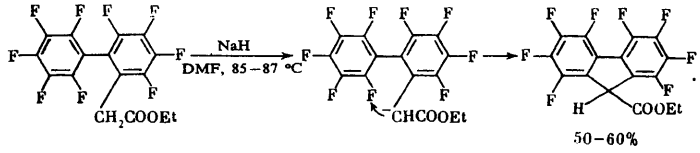


Fairly forcing conditions (100–135 °C) are required to carry out such reactions and then yields of substitution products are moderate (20–60%). However reactions proceeded as a rule at room temperature when using perfluoroarenes with electron-accepting substituents of the type of CN, CF_3 or $C(CF_3)_3$ but yields of products were significantly increased (70–85%).

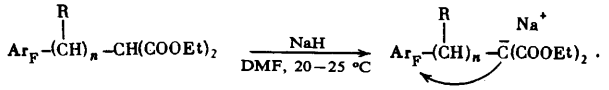
The polyfluoroarene-containing compounds obtained in this way were strong CH-acids. The carbanions corresponding to them, possessing a poorly screened reaction centre, are fairly active reactants in S_NAr type reactions and are used for example for the synthesis of perfluorinated benzhydryl derivatives.[149]



The anion of ethyl polyfluorinated diphenylacetate has been suggested for the synthesis of fluorinated fluorene.[151,152]

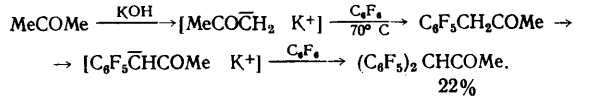


This example may be considered as a particular case of a general method of obtaining polyfluorinated carbocyclic compounds by the intramolecular nucleophilic substitution of a fluorine atom by aralkyl substituted malonic or cyanoacetic esters.[147]



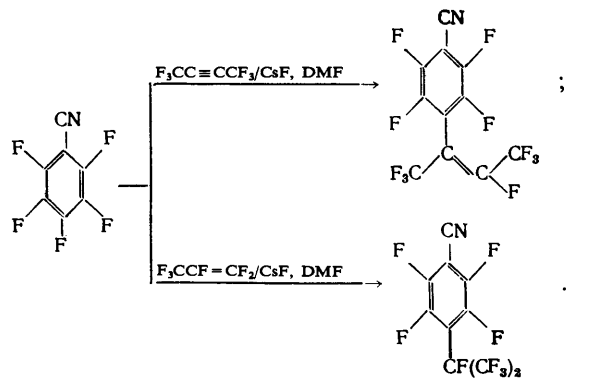
Derivatives of indane (n = 2), acenaphthene (n = 2) and 9,10-dihydrophenanthrene (n = 1, Ar = $C_6H_5C_6F_4$-2) were obtained in this way.[153,154]

Ambident anions may react with perfluoroarenes at both reaction centres. Thus anions of acetoacetic ester[155,156] and acetophenone[157] react with hexafluorobenzene and perfluorotoluene at a carbon atom with subsequent intramolecular cyclisation at oxygen with the formation of 4,5,6,7-tetrafluorobenzofurans (80–140 °C). At lower temperatures the reaction was successfully stopped at the *C*-arylation stage.[157,158]

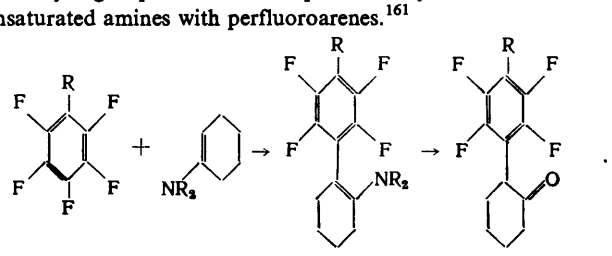


However depending on the nature of the substrate, solvent and enolate ion a mixture of *O*- and *C*-isomers or even predominantly the *O*-isomer may be formed. Thus replacement of fluoride ion by acetate or mesylate in octafluorotoluene leads preferentially to *O*-arylation of the potassium derivative of acetoacetic ester (DME, dimethylacetamide, EtOH).[122] On interacting the anion of pentafluoroacetophenone with $C_6F_5CF_3$ a mixture of *O*- and *C*-arylation products is formed the ratio of which depends on the nature of the solvent.[158]

The reaction of perfluoroaromatic compounds with perfluoroalkenes or alkynes in the presence of fluoride ion is of particular interest since it is a nucleophilic variant of the Friedel–Craft reaction.[103,159,160]



It is possible to obtain ketones, esters and amides containing a perfluoroaryl group in the α position by condensation of α,β-unsaturated amines with perfluoroarenes.[161]

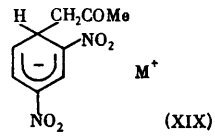


III. Preparation of anionic σ-complexes with C–C bonds

One further route to introduce a C–C bond into electron-deficient arenes comprises the preparation and oxidation of anionic σ-complexes, including 1,3-σ-complexes, containing good leaving groups of the halogen type in the aromatic ring.

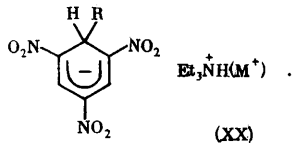
1. Reaction of aromatic compounds with carbanions and heteroorganic compounds

The simplest method of obtaining anionic σ-complexes of aromatic compounds containing electron-accepting groups (NO_2, CN, SO_2CF_3, etc.) with carbanions is the interaction of an aromatic substrate with a CH-acid in the presence of base. The possibility of forming stable complexes of such type was shown for the first time by Janovsky[162,163] in 1886 in the reaction of *m*-dinitrobenzene (*m*-DNB) with alkaline aqueous acetone. However only in 1963 was this σ-complex successfully isolated in the solid state[164] and its structure demonstrated.[165]



(XIX)

Historically most work is linked with the study of σ-complexes of nitroaromatic compounds with the acetonyl anion. Potassium carbonate,[166] alkali metal hydroxides and alkoxides[164,167–169] and amines[170,171] were used as bases for their preparation. The σ-complex of 1,3,5-trinitrobenzene (TNB) with acetonyl anion was obtained on carrying out the reaction in an acetone medium (~20–30 fold excess) in the presence of a twofold excess of KOH (spectro-photometric check). The yield of (XX) for R = CH_2COMe was 73%.[164]



(XX)

It was shown by PMR spectroscopy that in the presence of triethyl- or diethylamine TNB forms a σ-complex (XX) with various ketones which simultaneously serve as solvents [R = CH_2COMe, CH(Me)COEt, CH(Ph)$COCH_2Ph$, $CH(CH_2)_4CO$, $CH(CH_2)_3CO$,[170,171] $CH(CH_2)_5CO$, CH_2COPh], yield was 78%.[172]

These complexes may readily be isolated by precipitation with ether. With unsymmetrical ketones such as methylethylketone a mixture is formed of the isomeric complexes (XX) [R = CH_2COEt or CH(Me)COMe].[171] The exception was methylisopropylketone, in this case only one complex is formed of type (XX) (R = CH_2COPr-iso).[170]

To obtain complexes of TNB with anions of *para* substituted acetophenones XC_6H_4COMe (X = NO_2, OMe, CN) the reaction was carried out in dioxan in the presence of a large (~20 fold) excess of Et_3N.[172] In this case a twofold quantity of the CH-acid

was used (yields of complexes were not indicated). Complexes of TNB with anions of α-haloketones were obtained on carrying out the reaction in MeCN in the presence of Et_3N.[173]

The formation of adducts (XX) with anions of nitroaliphatic compounds [R = CH_2NO_2, $CH(Me)NO_2$, $CH(Et)NO_2$, $C(Me)_2NO_2$],[174] acetonitrile,[175] propionaldehyde[176] and phenylacetonitrile[170] was demonstrated by PMR spectroscopy. In all cases the reaction was carried out in the presence of a large excess of CH acid. The complex of TNB with nitromethane anion was isolated using NaH as base (yield was 35%).[177] An equimolar amount of CH-acid was applied to obtain the complex of TNB with the anion of acetylcyclopentadienylmanganese tricarbonyl which is formed in the presence of NEt_3 in a medium of MeCN (50% yield).[178]

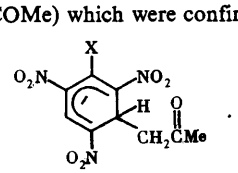
The alkali metal methoxides are effective bases for obtaining anionic σ-complexes.[168,169] Complexes of TNB with anions of acetone, cyclobutanone, cyclopentanone and cyclohexanone were isolated in quantitative yield on carrying out the reaction in a medium of the ketone.[169] To obtain complexes of TNB with cyanoacetic and malonic esters the same authors used an equimolar and double amount of the corresponding CH-acid, reaction was carried out in MeOH and yields of complexes were quantitative.[179] The σ-complexes of TNB with CCl_3 and CBr_3 anions were isolated in yields of 80 and 63%.[180] Reaction in these cases was carried out in DMSO with an excess (10 fold) of chloroform or bromoform in the presence of MeONa. The complex of TNB with the trichloromethyl anion was also formed from trichloroacetic acid and TNB in DMSO. The corresponding substitution product was isolated on oxidation of this complex with bromine in pyridine.[181]

It is known that acetoacetic ester reacts with TNB in the presence of various bases (KOH, Et_3N, MeONa) with the formation of a bicyclic complex (see Chapter III, section 3). However on interacting TNB with potassium-acetoacetic ester a complex of type (XX) [R = CH(COMe)COOEt] was also obtained in 33% yield.[182]

Finally σ-complexes of TNB with the anions of DMF, dimethylacetamide and DMSO were synthesised in the presence of KOH or Bu_4NOH in a dioxan medium. In each case the CH-acid was introduced in excess (yields of complexes were 40, 75 and 80% respectively).[183] The σ-complex of TNB with indole was obtained in 60–90% yield in the two-phase system $CH_2Cl_2-H_2O-NaOH$ in the presence of *N*-methylquinolinium, *N*-methylisoquinolinium or tetramethylammonium salts.[184]

As already mentioned a methyl group located in the *para* position to a nitro group in polynitro aromatic compounds may be deprotonated by the action of base in polar solvents (DMSO). The resulting carbanion reacts with TNB giving anionic σ-complexes.[185,186] On using equimolar amounts of CH-acid and KOH or MeONa as base complexes of TNB were isolated (yield ~50%) and characterised with anions of 2,4,6-trinitrotoluene,[185,186] 2,4-dinitrotoluene, 4,6-dinitro-*m*-xylene and 2,4,6-trinitro-*m*-xylene.[186] Addition of two molecules of TNB is possible (in an excess of base) for the latter.

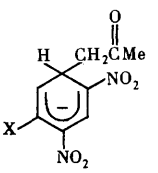
In the presence of Et_3N, MeONa or KOH 1-X-2,4,6-trinitrobenzene (X = OEt, OMe, OPh, Me, Cl, NMe_2, COOH, COOMe, SMe) reacts with acetone forming 1,3-σ-complexes (XXI) (R = CH_2COMe) which were confirmed by PMR spectroscopy.[98,187–189]



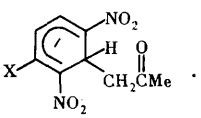
(XXI)

In contrast to ketones which form stable 1,3-σ-complexes with 1-X-2,4,6-trinitrobenzene, the stronger CH-acids such as acetoacetic, malonic, and cyanoacetic esters, and malondinitrile react with 1-X-2,4,6-trinitrobenzene (X = OMe, OCOMe, Cl, OAr) in the presence of MeONa giving 1,3-σ-complexes which rearrange into 1,1-σ-complexes with the subsequent formation of a substitution product.[52,88–90,100,101]

It is known that anionic complexes of *m*-dinitrobenzene (DNB) derivatives are far less stable than complexes of TNB. For example, the equilibrium constant of the complex of TNB with methoxide ion is 17 lit.mol^{-1} and for the complex of *m*-DNB with methoxide ion the equilibrium constant is only 1×10^{-6} lit.mol^{-1}.[190] As mentioned above the σ-complex of TNB with acetonyl ion was obtained in 73% yield on using KOH as base. Under the same conditions *m*-DNB gave a σ-complex in only 34% yield.[164] Similarly 1-X-2,4-dinitrobenzenes react in alkaline medium with acetone with the formation of the isomeric complexes (XXII) and (XXIII).



(XXII)

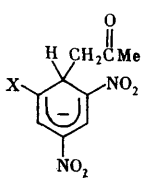


(XXIII)

A σ-complex (XXII) is mainly formed when X = H, OMe, COOMe, Cl, Br, I, Me, n-Pr, n-Bu, or SO_2Ph[99,164,191–193] but when X = F, SEt, SCN, or SPh a σ-complex of type (XXIII) predominates.[164,192,193] On carrying out the reaction in an acetone medium and using KOH as base the yield of complexes was 10–35% overall.[99,164,191–193,195] However on using alkali metal (Na, K, Rb, Cs) methoxides the yields of σ-complexes became almost quantitative.[167]

The σ-complexes of 2,4-dinitronaphthalene, 2,4,5,7-tetranitronaphthalene and 9-nitroanthracene with acetonyl and nitromethyl anions have been obtained and characterised.[174,187]

1-X-3,5-Dinitrobenzenes react in alkaline medium with acetone giving two isomeric products (XXIV) and (XXV). When X = OMe or Me only complexes (XXIV) were obtained in 7.5 and 18% yield in the presence of KOH.[194] A mixture of σ-complexes (XXIV) and (XXV) was formed when X = COOEt,[194,195] CF_3,[194–196] CN,[196] COOMe and COO^-,[197] $CONH_2$ and $CONMe_2$.[198]



(XXIV)



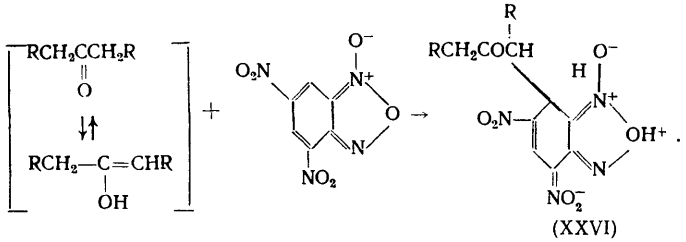
(XXV)

Isomerisation constants were measured for σ-complex (XXIV) going to (XXV), which had been obtained from the enolates of cyclohexanone and 1-X-3,5-dinitrobenzene [X = $CON(CH_2)_5$, COOMe, CN].[199]

Complexes obtained from 1,3,5-*tris*-(trifluoromethylsulphonyl)-benzene (TFMSB) proved to be several orders of magnitude more stable than complexes of TNB. The complex of TFMSB with

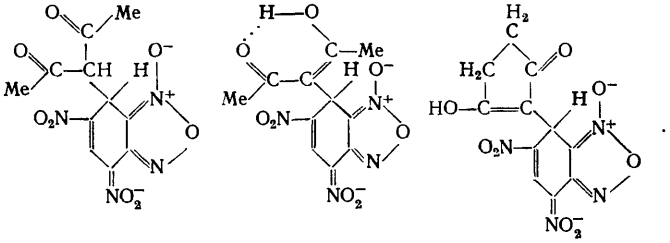
acetonyl anion using KOH in acetone as base was isolated in 24% yield[200] but on using EtOH the yield was 97%.[177] The complex of TFMSB with nitromethane anion was isolated (67% yield) using NaH.[177] Complexes of TFMSB with the anions of diethyl malonate and propionaldehyde were not isolated but were oxidised to the corresponding substitution products.[201]

4,6-Dinitrobenzofuroxan (DNBFX) and 4,6-dinitrobenzofurazan (DNBFZ) are even stronger electron-accepting substrates capable of forming anionic σ-complexes even in the absence of base. DNBFX reacts with water and methanol in the absence of base forming hydroxyl and methoxyl complexes and also with ketones. The formation of σ-complexes (XXVI) with anions of acetone, cyclopentanone, cycloheptanone, pentane-2,4-dione and 3-methylpentane-2,4-dione has been demonstrated.[202] It was proposed that reaction was effected with the enolic form of the ketone or with the enolate ion formed as a result of its partial ionisation.[202]



(XXVI)

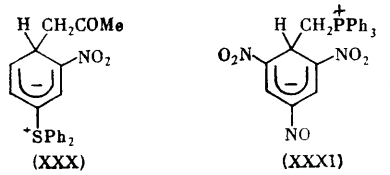
β-Dicarbonyl compounds like pentane-2,4-dione or cyclopentane-1,3-dione give adducts which may exist both in the ketonic (XXVII) and in the enolic forms (XXVIII) and (XXIX).[202]



(XXVII) (XXVIII) (XXIX)

Compounds DNBFX and DNBFZ form complexes even with such weak bases as 1,3,5-trimethoxybenzene (see also p. 765).[203]

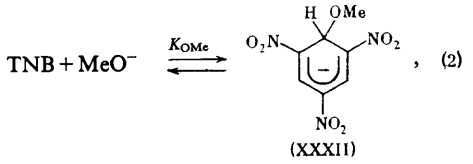
Zwitterionic σ-complexes (XXX) and (XXXI) were obtained by the reaction of an alcoholic solution of KOH with an acetone solution of *m*-nitrophenyldiphenylsulphonium fluoroborate[204] and methylenetriphenylphosphorane with TNB.[205]



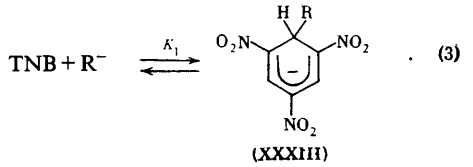
(XXX) (XXXI)

The kinetics of formation and stability constants of σ-complexes of TNB with appropriate carbanions have been studied for a series of CH-acids in the presence of MeONa.[179,90] The following scheme has been proposed for the formation of a σ-complex with a C–C bond where the limiting step is the addition reaction of carbanion to TNB [reaction (3)].

$$RH + MeO^- \overset{K}{\rightleftarrows} R^- + MeOH, \quad (1)$$



(XXXII)



(XXXIII)

Rate constants are given in Table 2 for the formation and dissociation (k_1 and k_{-1}) of σ-complexes of TNB and also the equilibrium constant (K_1). It is seen from the data given in Table 2 that the stability of σ-complexes falls as the strength of the CH-acid increases. It was reported[179] that TNB complexes with a C–C bond possess a higher stability than complexes with *O*-nucleophiles. The complex with acetone is more than 10 orders of magnitude more stable than the complex with methoxide. The anions of methyl acetate, methyl cyanoacetate, dimethyl malonate and malondinitrile are less basic than MeO^- but their complexes with TNB proved to be more stable than methoxyl [the equilibrium constant for the formation of complex (XXXII) K_{OMe} = 17 lit.mol^{-1} is comparable only with the equilibrium constant for the formation of the least stable complex of TNB with methyl acetoacetate]. The high stability of complexes with enolate ions is confirmed also by the low values for the decomposition rate constants of σ-complexes (in certain cases values of k_{-1} are so low as to be difficult to measure).[172]

Table 2. Kinetic and equilibrium parameters for the reaction of TNB with carbanions in methanol.[179]

Carbonyl compounds	K, lit. mol^{-1}	k_1, lit. mol^{-1}.sec	k_{-1}, sec^{-1}	K_1, lit.mol^{-1}
MeCOMe	10^{-6}	$3.30\cdot10^{6}$	$8.2\cdot10^{-6}$	$4\cdot10^{11}$
	10^{-4}	$1.62\cdot10^{5}$	$1.76\cdot10^{-4}$	$9.2\cdot10^{8}$
$CH_2(COOMe)_2$	0.5	$2.5\cdot10^{5}$	20.5	$1.22\cdot10^{4}$
$CH_2(CN)COOMe$	54	$1.3\cdot10^{5}$	62	$1.66\cdot10^{3}$
$CH_2(CN)_2$*	590	$3\cdot10^{5}$	$6.5\cdot10^{3}$	40
$MeCOCH_2COOMe$	418	$5.5\cdot10^{3}$	470	11.7

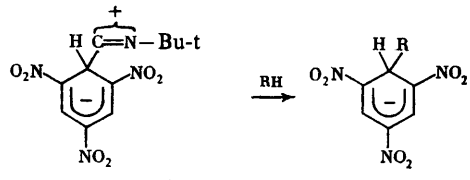
*Literature data.[90]

In the majority of the reactions described above the CH-acid which is a source of carbanion is taken in excess and frequently serves as solvent. The excess of CH-acid may be avoided if the

reaction is carried out in a two-phase system of solid base–solvent. At the same time the use of such a system makes it possible to extend significantly the limits of the pK_a of the CH-acids entering into the reaction. Thus in the system THF–solid base (KF, K_2CO_3, KOH)–18-crown-6 ether the σ-complexes of TNB with such radicals R as CH(Ph)COOEt(Me), CH(Ph)CN, C_6F_5 or fluorenyl were successfully obtained.[206] These complexes contain 1 mole 18-crown-6 ether in their composition. The complexes had been obtained previously by reactions with organomercury and organotin compounds.[207–210] The weakest CH-acid which reacts with TNB under these conditions (KOH as base, KF and K_2CO_3 proved to be ineffective) was pentafluorobenzene. Phenylacetylene (pK_a 29.4 in DMSO[211]) did not react with TNB even in the presence of KOH. It should be mentioned that the final result of the reaction depends not only on the base strength and on the CH-acid but also on the stability of the σ-complex (XXXII) of aromatic substrate with base, the formation of which often precedes the formation of a σ-complex (XXXIII) with the carbanion. For this reason KF proved to be a more effective base than K_2CO_3. The stability of the σ-complex formed with base may explain the fact that TFMSB, which significantly surpasses TNB in electrophilicity, reacts under PTC conditions only with fairly strong CH-acids, such as diethyl malonate, when, as for TNB, a σ-complex was obtained with anions of weaker acids such as phenylacetonitrile, ethyl phenylacetate, pentafluorobenzene or fluorene.[206]

Not only CH-acids but also organometallic compounds have been used to obtain σ-complexes. It was shown by PMR spectroscopy that organomercury compounds R_2Hg (or RHgX), where R = CH_2COMe, CH(Ph)COOEt, CCl_3, C_6F_5, $CH(CF_3)_2$ or *o*-carboranyl, react with TNB forming σ-complexes (XX) under conditions of nucleophilic catalysis with iodide ion.[207,208] Some organotin compounds $RSnMe_3$, where R is acetonyl, fluorenyl, indenyl or cyclopentadienyl also successfully react with TNB. In this case the solvent DMSO played the role of nucleophilic catalyst.[209,210]

It has been shown possible to use organocopper and organotin compounds for the synthesis of σ-complexes with TNB. Reactions of TNB with phenyl- and 2,6-dimethoxyphenylcopper,[212] 2,6-dimethoxy- and 2,4,6-trimethoxyphenylsilver,[213] copper and silver phenylacetylides,[214] hexenylcopper,[214] 2-furyl- and 2-thienylcopper,[215] acetylcyclopentadienylmanganese tricarbonylsilver,[216] cyclopentadienyl- and indenylsilver[217,218] occur at room or lower temperatures in pyridine or quinoline. Organocopper compounds proved to be somewhat more reactive than silver derivatives. The σ-complexes were isolated in some cases[212,213,215–218] and were oxidised to the corresponding substitution products (see chapter III, section 5). The interesting σ-complex (XXXIV) was obtained from TNB and t-BuNC in the presence of copper or Cu_2O.[219] Complex (XXXIV) was unstable and reacted with CH-acids with the formation of σ-complexes with CCl_3, indenyl, and cyclopentadienyl anions.



(XXXIV)

Organosilicon compounds $RSiMe_3$ also react with TNB with fluoride ion catalysis. These were of various types, benzyl and allyl derivatives, silylated ketones, ethers and acylsilanes (pK_a of the corresponding RH was 20–35) and form ionic σ-complexes in good and occasionally quantitative yield.[220,221]

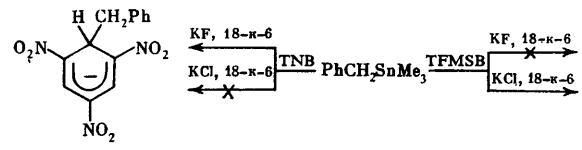
$$TNB + RSiMe_3 \xrightarrow[THF]{KF,\ 18\text{-}K\text{-}6} [TNB.R']K^+.(18\text{-}K\text{-}6),$$

$$R = \bigcirc\!\!-O-,\quad R' = \bigcirc\!\!=O,$$

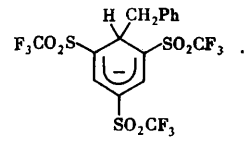
R = R′=CH_2COOMe, CH_2COOEt, CH_2COEt, COPh, COMe, CH_2Ph, All, C≡CPh.

It should be mentioned that organosilicon reagents have proved to be useful in the synthesis of various σ-complexes which are difficult to obtain by other routes, such as σ-complexes with alkyl (CH_2Ph, $CH_2CH=CH_2$) and acyl (COMe, COPh) groups. The application of organosilicon compounds has enabled the selective introduction of the trinitrophenyl group into unsymmetrical ketones while the reaction of TNB with these ketones in the presence of base gives a mixture of isomers. In certain cases, for example when obtaining complexes $[TNB.C{\equiv}CR]^-$ and $[TNB.\overline{CH-(CH_2)_4-CO}]^-$, the use of $RSiMe_3$ is more convenient than CH-acids or organo-silver or copper compounds and gives better yields.

TFMSB, in contrast to TNB, reacts under conditions of catalysis by fluoride ion only with the most reactive of the $RSiMe_3$ studied, viz. the trimethylsilyl ether of cyclohexanone enol. In all the remaining cases the reaction stops at the stage of forming an anionic σ-complex with fluoride ion. It was mentioned above that the same result was observed in reactions of TFMSB with CH-acids. In the presence of fluoride ion TFMSB does not form a σ-complex with a C–C bond even with $PhCH_2SnMe_3$, while TNB reacts readily, giving complex (XXXV). However to obtain the σ-complex of TFMSB with a $PhCH_2$ group (XXXVI) it was sufficient to replace fluoride ion by chloride ion which also forms a complex with TFMSB but is undoubtedly less stable than the complex with fluoride. It has been reported that complex (XXXV) was not formed in the reaction of TNB with $PhCH_2SnMe_3$ in the presence of KCl.[211]



(XXXV)

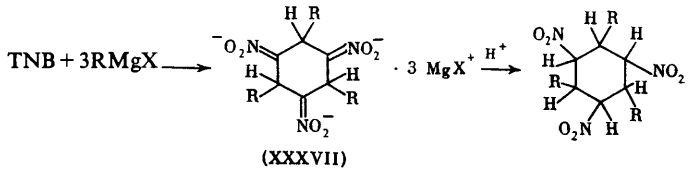


(XXXVI)

Organosilicon compounds have also been proposed for introducing C–C bonds into 1-X-2,4-dinitrobenzenes. However the complexes formed were less stable than complexes of TNB and their oxidation was carried out without isolation (see p. 763–764).[222]

Organolithium and organomagnesium compounds are used as a carbanion source for CH-acids with pK_a 30–33. However TNB adds three molecules of RMgX on carrying out the reaction in ether

or THF giving 1,3,5-trialkyl-2,4,6-trinitrocyclohexanes [the intermediate (XXXVII) was not identified] on acidification of the reaction mixture.[223,224]



(XXXVII)

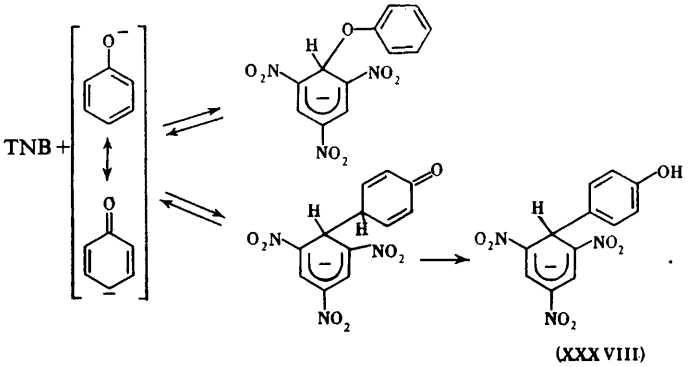
R = Me, Et, n-Pr, n-Bu, iso-Bu.

The reaction of RMgX with *m*-DNB, 1-chloro-2,4-dinitrobenzene and 2,4-dinitroanisole proceeds in a similar manner.[225] However in the majority of cases the reaction of organolithium and organomagnesium compounds with polynitroaromatic compounds gives a mixture of products of oxidation-reduction reactions and addition reactions at the nitro group. Consequently it is a fairly complex problem to obtain anionic σ-complexes from weak CH-acids (pK_a > 30–33). Taylor has succeeded in obtaining σ-complexes of TNB with methyl and n-butyl groups using the appropriate tetraalkylboron salts $Alk_4B^-Me_4N^+$ (or Ph_4As^+).[226]

σ-Complexes with Me_3ECH_2-groups, where E = Si, Sn or Ge, were obtained in a similar manner.[227] On using tetraalkylammonium salts $(CH_2EMe_3)_4B^-Me_4N^+$ σ-complexes of TNB with Me_3ECH_2-groups were successfully obtained while the use of lithium salts, such as Me_3SiCH_2Li or $(Me_3SiCH_2)_4BLi$, led to a mixture of unidentified products.[227]

2. Reaction with phenoxide ions and nitrogen bases

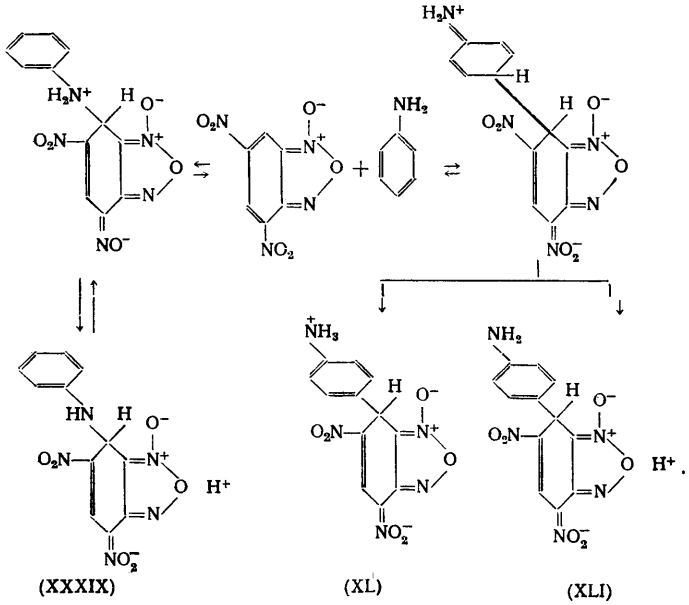
The ability of phenols and aromatic amines to act as *C*-nucleophiles in reactions of the S_NAr type in the presence of base was recorded in Chapter II. Phenoxide ions, anions of nitrogen heterocycles and anilines, in the presence of NEt_3 or 1,4-diazabicyclooctane, also form σ-complexes with C–C bonds in several cases,[228–234] and therefore may be used to introduce homo- or heterocyclic radicals containing strongly electron-donating substituents into electron-deficient aromatic substrates. In the reactions of phenols σ-complexes with C–O bonds are usually the reaction products under kinetic control and then rearrange into complexes with C–C bonds, the reaction products under thermodynamic control.[234]



(XXXVIII)

Adduct (XXXVIII) was obtained by the reaction of TNB with PhOH in DMSO or in DMSO–MeOH in the presence of MeONa (80% yield).[231] A small quantity of the corresponding *ortho* isomer was formed in addition to the *para* isomer (XXXVIII) and was detected by PMR spectroscopy.[231] A bond was formed in the *ortho* position in the complex of TNB with the anion of α-naphthol.[232]

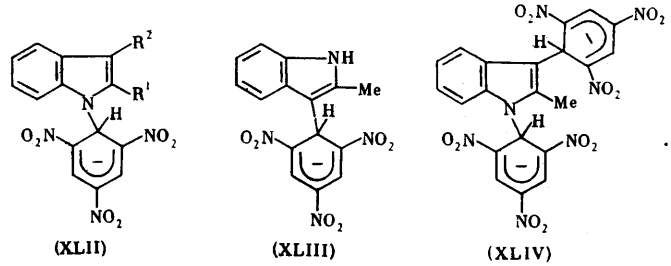
In contrast to phenoxide ion, aniline gives only a complex with a C–N bond with TNB in the presence of Et_3N or 1,4-diazabicyclooctane.[235,236] However with a more strongly electron-deficient substrate like DNBFX, depending on the experimental conditions, it is possible to obtain both a complex with a C–N bond (XXXIX) and a σ-complex with a C–C bond (XL) or (XLI).[237–240] Only complex (XLI) is formed when using equimolar amounts of aniline and DNBFX. The application of a two fold excess of $PhNH_2$ leads to a mixture of products (XXXIX) and (XLI) but on adding Et_3N only complex (XXXIX) was isolated and was established by PMR spectroscopy.[238]



(XXXIX) (XL) (XLI)

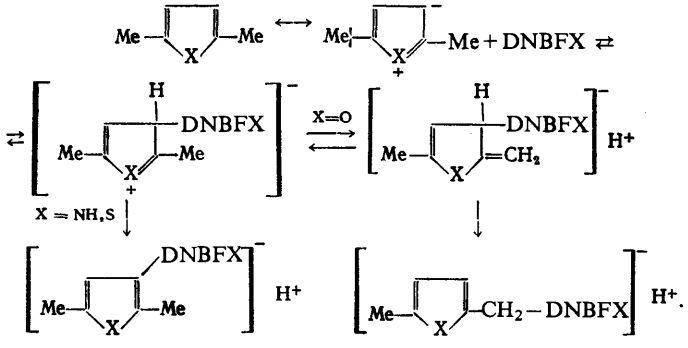
1,8-*bis*-(Dimethylamino)naphthalene reacts with DNBFX or 4,6-DNBFZ giving an adduct of the type of (XLI) in quantitative yield.[241,242]

TNB reacts with nitrogen heterocycles in the presence of base forming a mixture of complexes with C–N and C–C bonds the stability of which is determined by the nature of the heterocycle.[231–234,243–246] Thus 3-methyl- and 2,3-dimethylindoles in DMSO in the presence of MeONa give only complexes with a C–N bond (XLII), while with TNB 2-methylindole forms a mixture of complexes (XLII)–(XLIV) with a predominance of complex (XLIII) which, after some time, becomes the sole product.[243]



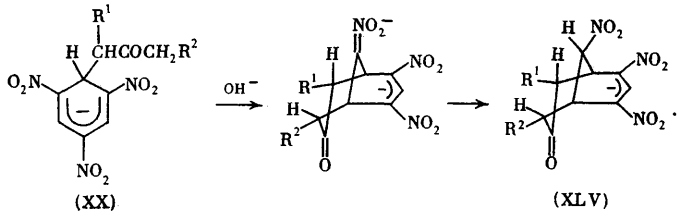
(XLII) (XLIII) (XLIV)

Compounds DNBFX and DNBFZ are also capable of reacting with nitrogen heterocycles in the absence of base.[247–249] Only complexes with C–N bonds are formed with imidazole or with *N*-alkylimidazole and only complexes with C–C bonds are formed with pyrrole, indole, thiophen and their *N*-alkyl substituted derivatives. However a methyl group proved to be more reactive in 2,5-dimethylfuran.[249]



3. Formation of bi- and tricyclic complexes

As mentioned above, the σ-complexes of TNB with anions of ketones are fairly stable. However, in the presence of strong bases such as KOH or NaOH they may be subject to further conversion generally forming bicyclic adducts (XLV).[250]



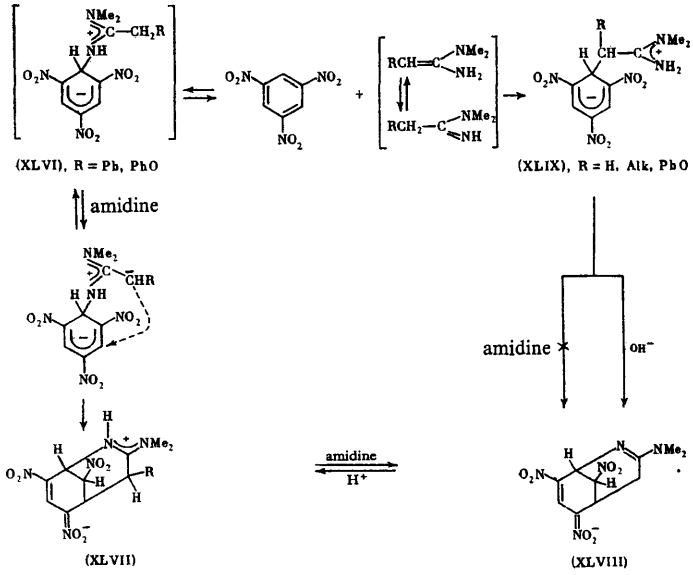
(XX) (XLV)

The reaction stopped at the stage of forming σ-complex (XX) o using Et_3N as base.[170,171] It is interesting that bicyclic adducts wer formed on interacting TNB with ketones in the presence c diethylamine (Et_2NH) although the basicities of Et_3N and Et_2NH are close.[251] It was considered that the corresponding enamines added to TNB in this case.[252] A tricyclic complex was obtained from cyclohexanone in the presence of Et_2NH while cyclopentanone gave the usual σ-complex (XX) with R = $\overline{CH-(CH_2)_3-CO}$.[253]

The only result of interacting TNB with β-dicarbonyl compounds in the presence of Et_3N were bicyclic adducts of the (XLV) type. Complexes of type (XX) were not isolated.[15,254–258] 1-Cyano-3,5-dinitrobenzene, methyl 3,5-dinitrobenzoate, methyl 2,4,6-trinitrobenzoate, picryl amide and picric acid react with β-dicarbonyl compounds (acetoacetic ester, 1,3-dicarbomethoxyacetone) in a similar manner.[254,255,259] Bicyclic products were also formed on interacting 1,3-dicarbomethoxyacetone with dinitro- and tetranitronaphthalenes.[255]

Recently the reaction of nitro aromatic compounds with amidines has been studied intensively.[260–264] The products of these reactions may be of considerable interest to pharmacologists.[260] Generally it is possible to form several complexes (XLVI)–(XLIX) by reacting TNB with amidine (Scheme 1).

Scheme 1



(XLVI), R = Ph, PhO (XLIX), R = H, Alk, PhO

(XLVII) (XLVIII)

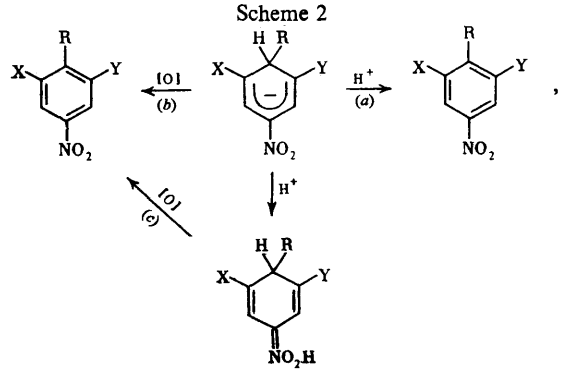
Although the formation of adduct (XLVI) was not confirmed by PMR spectroscopy it was proposed that this particular σ-complex was a precursor in the formation of bicyclic adduct (XLVIII). This conclusion was drawn on the basis that the alternative σ-complex (XLIX), which may occasionally be isolated together with bicyclic product (XLVII), is not converted into (XLVIII) by the action of amidine.[260,262] Complex (XLIX) may be converted into a bicyclic adduct, however it was necessary to apply a stronger base, such as KOH, to carry out the conversion.[261]

Adducts analogous to (XLVIII) were also formed from 1,3-dinitro- and 1,3,6,8-tetranitronaphthalene.[262] With a less strongly electron-deficient substrate, viz. 1-cyano-3,5-dinitrobenzene, no bicyclic adduct was formed.[263] It should be mentioned that products of intramolecular attack by the oxygen atom with the formation of bicyclic adducts were not detected.[253]

4. Oxidation of anionic σ-complexes

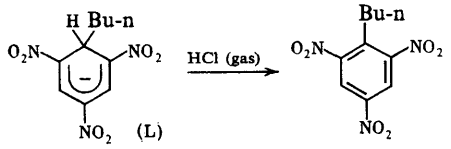
Products of substitution of hydride ion may be obtained from anionic σ-complexes by one of the methods given in Scheme 2:

Scheme 2



(a) action of acid on the σ-complex, (b) oxidation of the σ-complex, (c) protonation of the σ-complex to a nitronic acid with its subsequent oxidation.

It was shown by PMR spectroscopy that 1-n-butyl-2,4,6-trinitrobenzene was formed quantitatively on passing gaseous HCl into a solution of σ-complex (L) in CD_3CN.[226]

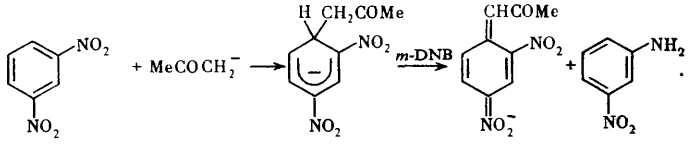


2,4-Dinitrophenylacetone (24%) was isolated on acidifying the Janovsky σ-complex (XIX)§.[265]

On acidification of solutions of anionic σ-complexes there usually occurs either decomposition into starting materials or the formation of nitronic acids which may then be converted into substitution products by the action of a suitable oxidising agent [route (c)]. Substitution products from σ-complexes of TNB with indenyl, cyclopentadienyl,[217,218] 1,3-dimethoxyphenyl,[213] thienyl and furyl[215] groups have been obtained in the same way.

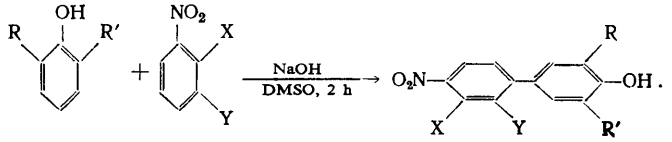
Most frequently σ-complexes are oxidised directly [route (b)]. It has been shown[218] that product yields on oxidation of σ-complexes of TNB (R is indenyl, cyclopentadienyl) with 1,4-benzoquinone or H_2O_2 were somewhat lower than on using method (c) [2,4,6-trinitrophenylcyclopentadiene was obtained in 80% yield by method (c) and in 52% yield by method (b)].

Occasionally the role of oxidising agent may be fulfilled by the initial nitroaromatic compound. Such a situation is brought about in, for instance, the known Zimmerman reaction.



The presence of *m*-nitroaniline among the reaction products supports this scheme.[266,267] A similar case has been described.[63]

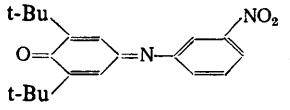
The reaction of *m*-DNB and of *m*- and *o*-cyanonitrobenzenes with 1,6-dialkylphenols (Alk = t-Bu or Me) in alkaline medium leads to a diaryl (28–69% yield). In the case of an unsubstituted phenol the yield of products fell to 17%. Mononitro compounds (nitrobenzene, 2-nitroacetophenone, 9-nitroanthracene) react differently with phenols but TNB forms only a σ-complex.[63]



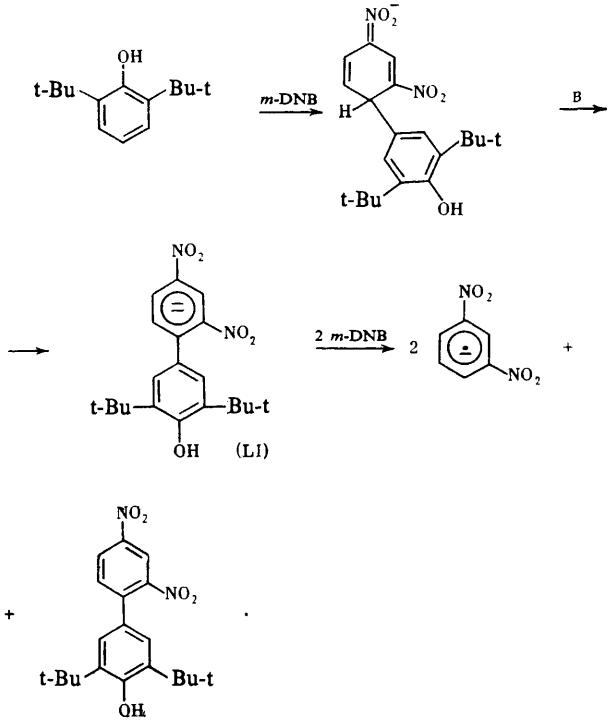
R, R′=Alk; X=H: Y=NO_2, CN; X=CN: Y=H.

§The formation of substitution products has also been recorded in other cases. However their yields did not exceed 10–15%.[188,214]

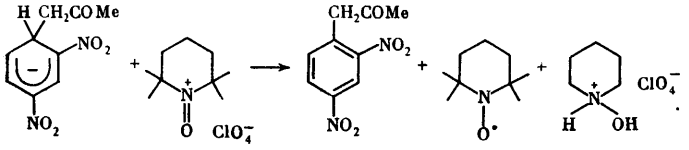
It is possible that the reaction mechanism comprises formation of a σ-complex and subsequent oxidation of it by nitroarene to the diaryl.[63,268] The imine



was detected among the products of reaction with *m*-DNB, i.e. reduction of the nitro compound occurred during the course of the reaction.[63]

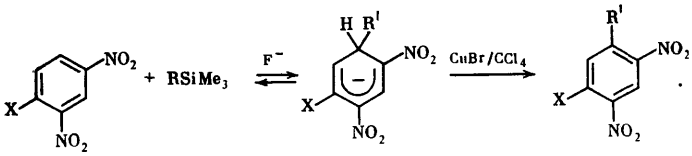


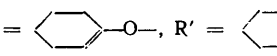
The oxidation[269] of the Janovsky complex to 2,4-dinitrobenzylmethylketone by manganese(III) acetate (yield not stated) and by *N*-oxopiperidinium perchlorate (80%) has been effected.[270]

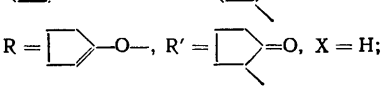


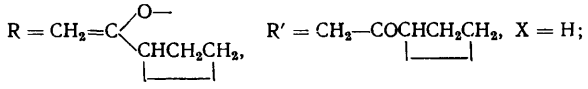
Using as example the σ-complex of *m*-DNB with cyclohexanone anion it was shown that it was possible to apply other oxidising agents such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDBQ), $(NH_4)_2Ce(NO_3)_6$, Br_2 in hexane or $CuBr_2$ in DMF, to the oxidation of complexes of DNB. Systems containing a catalytic amount of CuBr (or $CuBr_2$)/CCl_4 in MeCN also proved to be no less effective. These systems have been used for the oxidation of σ-complexes of

1-X-2,4-DNB obtained *in situ* from organosilicon compounds in the presence of fluoride ion.[222]



R =  , X = H, Cl, I, Me;





$R = R' = CH_2COOEt$, X = H;

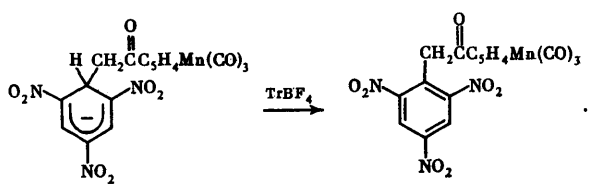
$R = R' = CH_2Ph$, X = H;

$R = R' = CH_2CH{=}CH_2$, X = H.

The effectiveness of the $CuBr/CCl_4$ system was confirmed by an experiment on the oxidation of the isolated and characterised Janovsky complex. The yield of 2,4-dinitrobenzylmethylketone was 80%,[222] i.e. the same as on oxidation with *N*-oxopiperidinium perchlorate.[270]

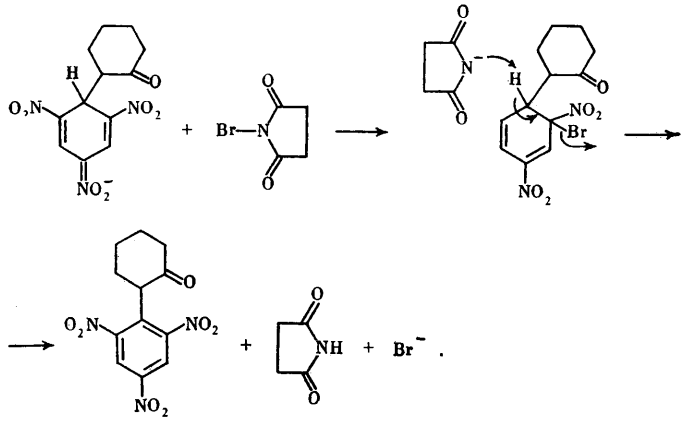
The oxidation of σ-complexes of TNB has been most widely studied. Various organic and inorganic compounds have been proposed as oxidising agents, the use of the latter is convenient and economical due to their availability. In addition the use of inorganic reagents simplifies, as a rule, the isolation of reaction products. The indisputable advantage of organic oxidising agents is their effectiveness. Chloranil, 2,3-dichloro-5,6-dicyanobenzoquinone, tropylium fluoroborate, *N*-oxopiperidinium perchlorate, and *N*-bromosuccinimide (NBS) are used most successfully in the oxidation of σ-complexes.[269–272] $FeCl_3$, $AgNO_3$, $(NH_4)_2Ce(NO_3)_6$, H_2O_2, $Pb(OAc)_4$, and solutions of halogens in water or organic solvents (Py, t-BuOH) are the inorganic reagents applied to the oxidation of σ-complexes.[180,181,271] It should be mentioned that the oxidation of the σ-complex $[TNB.CH_2COMe]^-K^+$ is the only one that has been widely studied. This complex is oxidised in an excellent manner by practically any oxidising agent. In the majority of cases it is seemingly impossible to predict which oxidising agent will prove to be most effective.[221]

It is known that the σ-complex of TNB with acetylcyclopentadienylmanganese tricarbonyl anion is oxidised by tropylium fluoroborate forming the substitution product in 80% yield, however on oxidation with trityl (Tr) fluoroborate a TNB derivative is formed.[178]



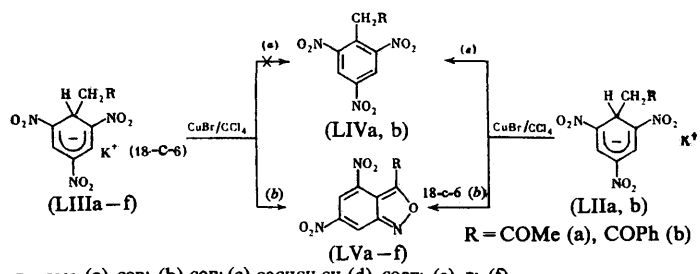
The complexes $[THB.CHal_3]^-$ (Hal = Cl, Br)[128,129] and complexes of TFMSB with $R = CH_2COMe$, $CH(COOEt)_2$, CH_2NO_2, $CH_2C(O)H$[201] were oxidised by solutions of bromine or chlorine in pyridine or t-BuOH.

NBS has been used successfully as oxidising agent for complexes of TNB with anions of ketones.[221,272] The reaction probably occurs in the following manner.



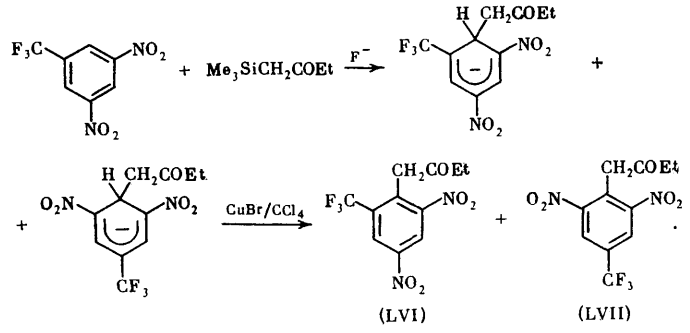
This mechanism was proposed on the basis of data obtained on the oxidation of the σ-complex of TNB with amidine.[20,264] Isoxazoline *N*-oxides are formed on oxidation of bicyclic complexes of TNB and β-dicarbonyl compounds with an excess of NBS.[273] *N*-Bromosuccinimide proved to be an effective oxidising agent for several other σ-complexes such as $[TNB.R]^-K^+$.18-crown-6 ether, where R = $CH(CH_2)_4CO$, COMe, COPh, or CH_2Ph.[221] A two fold excess of NBS was required for the oxidation of the σ-complex of TNB (XX) with R = CH_2COOMe when the methyl ester of (2,4,6-trinitrophenyl)bromoacetic acid was formed in 60% yield.[221] To obtain trinitrophenylacetic acid ester $(NH_4)_2Ce(NO_3)_6$ was used as oxidising agent. This reagent also proved to be effective for the oxidation of σ-complexes of TNB with R = C_6F_5, CH_2COEt. When R = All and C≡CPh the use of Cl_2O in CCl_4 has been proposed since the oxidising agents listed above proved to be ineffective.[221]

An unexpected result was obtained on oxidising σ-complexes with the system $CuBr/CCl_4$.[274] On oxidising σ-complexes (LII) where R = CH_2COMe and CH_2COPh substitution products (LIV) were formed. However if the oxidation was carried out in the presence of 18-crown-6 ether (18-c-6) then in place of the expected products (LIV) derivatives of 4,6-dinitrobenzisoxazole (4,6-dinitroanthranil) (LVa–f) were formed (30–70% yield). The result did not depend on whether the reaction was carried out with σ-complexes (LVa–f), whether the content of 18-c-6 was known, or the crown ether was introduced into the reaction mixture simultaneously with $CuBr/CCl_4$ and with complexes (LIIa,b). A necessary condition for such a conversion was the presence of a CH_2R group at the geminal point of the σ-complex.

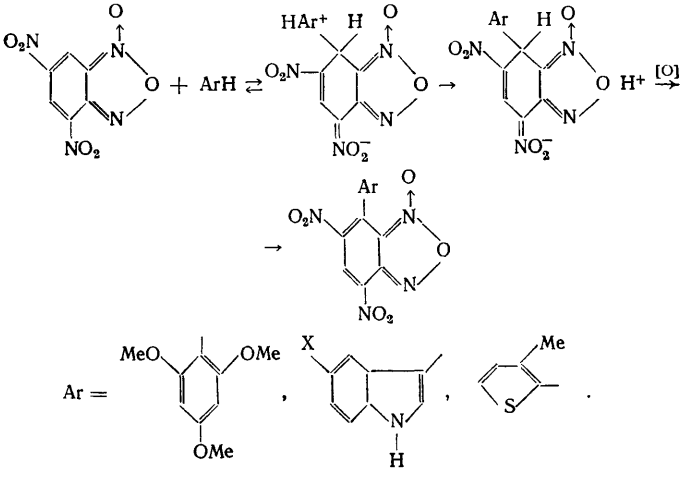


R = COMe (a), COPh (b)

Finally there is one further requirement, viz. the presence of three nitro groups in the aromatic nucleus, for anthranil formation. On oxidation of the σ-complex of 3,5-dinitrobenzotrifluoride only substitution products (LVI) and (LVII) were isolated (1 : 1).

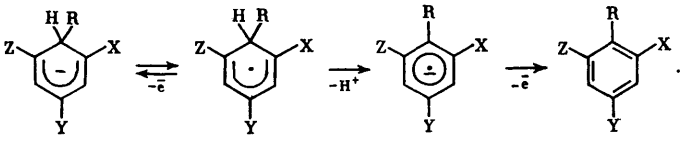


It is interesting that complexes of DNBFX and DNBFZ containing proton as counter ion were capable of spontaneous oxidation in DMSO. This ability is lost on replacement of H^+ by the cation of a metal such as Ag^+.[203]



This observation is all the more astonishing since such complexes are oxidised only by fairly strong oxidising agents such as $KMnO_4$.[203]

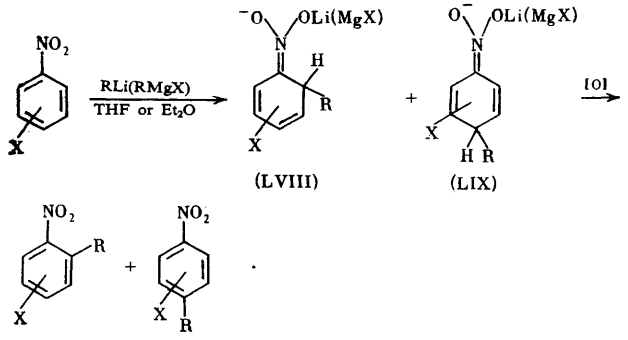
The electrochemical oxidation of acetone complexes of *m*-DNB, TNB and TFMSB and also the complexes of TNB and TFMSB with nitromethane anion has been studied.[177,269,275] It was shown that electrochemical oxidation of σ-complexes proceeds in one irreversible two-electron step and the oxidation potentials of the σ-complexes of TNB (0.82 – 0.92 V) were significantly greater than that of the complex of *m*-DNB (0.33 V) and lower than the oxidation potentials of σ-complexes of TFMSB (1.37 – 1.60 V). The oxidation potentials of σ-complexes increased in the same order as their thermodynamic stabilities. The following scheme was proposed for the oxidation of anionic σ-complexes.



IV. Alkylation of mononitro aromatic compounds

1. Reactions with organometallic compounds and with carbanions

The action of strongly basic organolithium and organomagnesium compounds on nitroarenes usually forms a complex mixture of products of oxidation-reduction reactions and of addition at the nitro group.[5,276–285] It was shown only comparatively recently that this reaction may be successfully applied to the synthesis of various alkyl nitro aromatic compounds if it is carried out at low temperature (–30 to 0 °C) and the reaction mixture is treated with suitable oxidising agents, reducing agents or acids literally a few minutes after mixing the reagents.[286–304] It is evident that unstable σ-complexes like (LVIII) and (LIX) (products of 1,4- and 1,6-conjugated addition) are formed in the reaction of RLi or RMgX with a nitroarene.[289]



The process is reversible if an equimolar ratio of reactants is used, a significant amount of nitro compound is recovered unchanged after the reaction. Best results were obtained using a two fold excess of RMgX. The reversibility of the reaction was also confirmed by the fact that the ratio of adducts (LVIII) and (LIX) changed with time. In the reaction of *o*-nitrotoluene with AlkLi the ratio of products (LVIII) : (LIX) = 1 : 4 after 1 h and 3 : 4 after 5 h.[289,298]

Adducts (LVIII) and (LIX) must be oxidised to obtain nitro alkylaromatic compounds. DDBQ, Br_2, O_2, $Na_2[Fe(CN)_6]$, $KMnO_4$, and $Pb(OAc)_4$ have been used as oxidising agents.[287,289–292] DDBQ is probably the most effective of them, but because of its high cost and poor availability its use is expedient in exceptional cases when a chemoselective oxidising agent not affecting other groups is required.[290,291]

In many cases good results were achieved using $KMnO_4$ in alkaline aqueous acetone.[289] The alkylated derivatives of nitrobenzene, naphthalene and several heterocycles were obtained in this way. $Pb(OAc)_4$ proved to be more effective for the oxidation of adducts of RMgX with polycyclic nitro compounds.[292] It should be mentioned that high yields of oxidation products (70 – 71%) were successfully achieved only for bi- and tricyclic compounds,[287,289,292] i.e. when adducts of type (LVIII) and (LIX) are fairly stable. In the case of nitrobenzene yields did not exceed 50%.[287,289] This is odd, extremely low yields were obtained on alkylating *m*-DNB (5%) and 2,4-dinitrotoluene (12%) (see however pp. 763 – 764).[287]

A comparison has been carried out of the effectiveness of various oxidising agents in relation to the adduct of 2-methyl-1-nitronaphthalene with BuLi (LX) (Table 3).[287] As is evident from the data in Table 3 DDBQ and Br_2 proved to be comparable in effectiveness for this system.

It is interesting that the nitro group is replaced by halogen on oxidation of adducts of type (LVIII) and (LIX) by hypohalites in alkaline medium.[293,294] Thus on treatment of adduct (LXII) with an alkaline solution of hypobromite the dihydro-isomer (LXIII), with bromine and the methyl group in *trans* configuration, is formed in high yield.

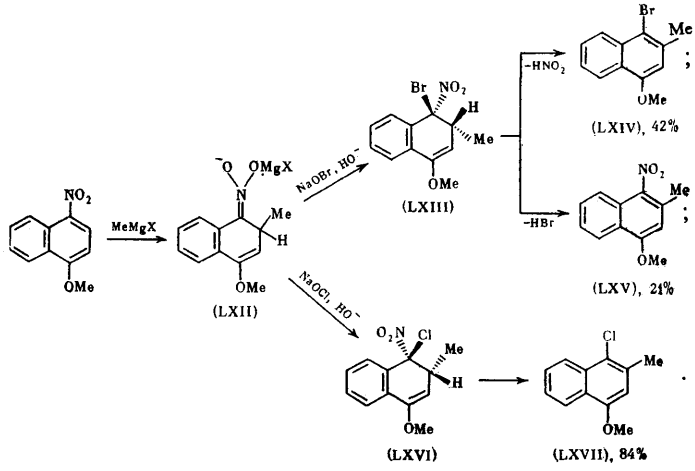
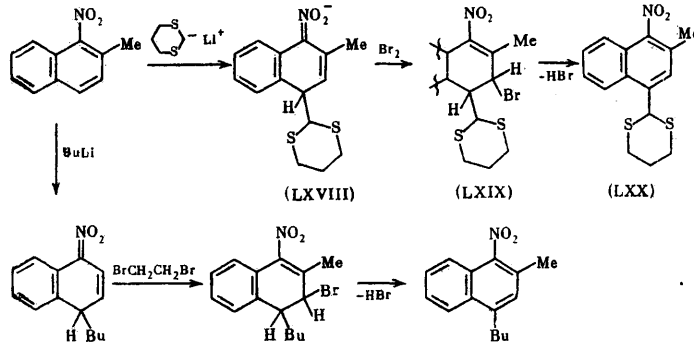


Table 3. Yields of 1-butyl-2-methyl-4-nitronaphthalene (LXI) obtained by the oxidation of adduct (LX) by various oxidising agents.

Oxidant	Solvent	Yield (LXI), %	Oxidant	Solvent	Yield (LXI), %
DDBQ	Ether	75	$Na_3[Fe(CN)_6]$	Ether	40
Br_2	Ether	70	$BrCH_2CH_2Br$	Hexane	26
O_2	Hexane	30			

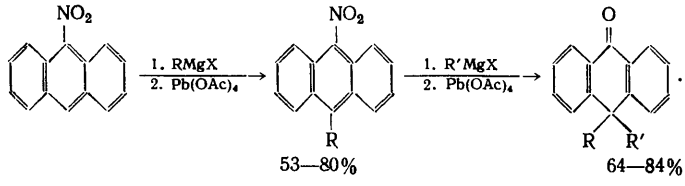
The adduct (LXIII) eliminates HNO_2 in alkaline medium (E_2 type process). The *trans* elimination occurs more readily than *cis* elimination (HBr) which also determines the predominant formation of product (LXIV) [ratio (LXIV):(LXV) = 2:1].[288,294] On replacing bromine by the poorer leaving group chlorine, i.e. on oxidising compound (LXII) with hypochlorite, the chloro derivative (LXVII) was formed exclusively.[293,294] The latter reaction was used for the synthesis of several chloro alkylarenes.[293]

It has been proposed that bromination of the nucleus occurs, albeit partially, on oxidation of adducts of type (LVIII) and (LIX) with bromine or dibromoethane. Subsequently aromatisation of the intermediate compound takes place by elimination of HBr.[287] In reality compound (LXIX) was isolated in 50% yield on oxidation of adduct (LXVIII) with bromine. On treatment with Et_3N, HBr was eliminated and (LXIX) was converted into the oxidation product (LXX).

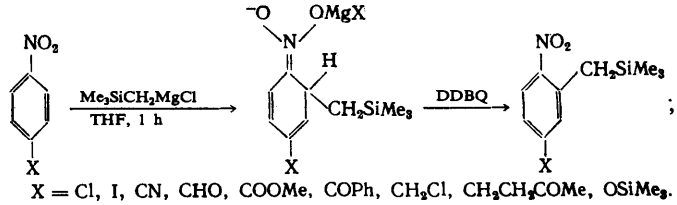


Other valuable compounds may be obtained from adducts (LVIII) and (LIX), such as nitroso alkylarenes (by treatment with BF_3 or concentrated HCl),[290,295–297] amines and hydroxylamines [by the action of an excess of RMgX and catalytic amounts of CuI or phosphorus(III) compounds].[298,299] A good method of obtaining arylamines is the reduction of adducts (LVIII) and (LIX) with hydrides ($LiAlH_4$ or $NaBH_4$) in the presence of catalytic amounts of Pd/C (–30 °C, ~20 min, 30–75% yield).[300]

It should be mentioned that the reaction of RM with nitroarenes is extremely regioselective. When a substituent such as OMe, OAr, SMe, SPh, Cl or F is present in the *ortho* or *para* position of a nitroarene an alkyl group R will enter almost exclusively at the unsubstituted position.[288,290] However when alkyl substituents are present a mixture of 1,4- and 1,6-addition products are formed in the ratio 2:1.[288,297] This special feature may be used for alkylating 1-R-2-naphthalenes at the C-1 atom[301] or for the two step synthesis of 10-R-10-R'-anthrones from 9-nitroanthracene.[292]



The reaction of nitroarenes with Me_3SiCH_2MgCl has been proposed for the synthesis of organosilicon compounds of the benzyl type.[302,303] The high regio- and chemoselectivity of this reaction enables the preparation of benzyl compounds of silicon containing such substituents as halogens, carbonyl and cyano groups.[303] Yields of products were 53–80%.

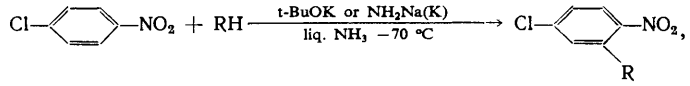


X = Cl, I, CN, CHO, COOMe, COPh, CH_2Cl, CH_2CH_2COMe, $OSiMe_3$.

Reaction in this case was carried out with a stoichiometric amount of RMgX and, as a rule, at low temperature (–70 to 0 °C). DDBQ proved to be the best oxidising agent, however oxidation has been carried out with $KMnO_4$.[302] The same high yields of organosilicon compounds were obtained in the reaction of Me_3SiCH_2MgCl with homo- and heterocyclic nitroaromatic compounds of naphthalene, quinoline, indole and anthracene.[303]

In contrast to alkyl magnesium chloride, allyl magnesium chloride gives adducts with 1,2-addition at the nitro group with $ArNO_2$, treatment of which *in situ* with $LiAlH_4$ in the presence of catalytic amounts of Pd/C leads to *N*-allyl-*N*-arylhydroxylamines or *N*-allylanilines.[304]

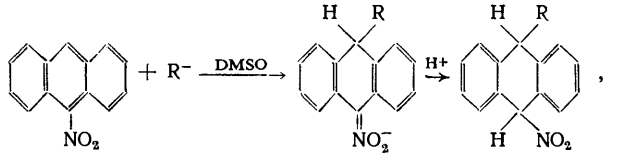
As already mentioned the reaction of mononitroarenes is reversible even with RLi or RMgX which is all the more remarkable since nitroarenes react with fairly stable carbanions (pK_a 20–12 for the corresponding CH-acid) in liquid NH_3.[305-306]



R = CH_2COMe, CH_2COBu-t, CH_2COPh, CH_2CN, CH_2COOBu-t.

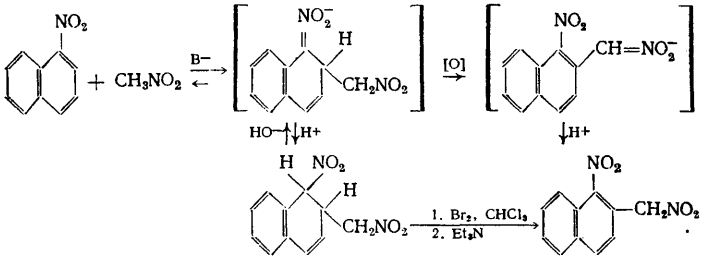
The oxidising agent is evidently partially *n*-$NO_2C_6H_4Cl$ itself and partially O_2 since the yields of substitution products (22–62%) were reduced on carrying out the reaction in an inert atmosphere.

It is possible to isolate the corresponding dihydro derivatives in good yield in the case of 1-nitronaphthalene and 9-nitroanthracene.[307]



R=CH $(COOEt)_2$, C (Me) $(COOEt)_2$, CH $(CN)_2$, Me_2CNO_2.

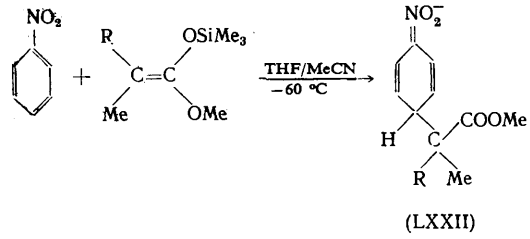
Nitromethane reacts with 1-nitronaphthalene in DMSO in the presence of NaOH forming an anionic σ-complex which may be oxidised directly or through the step of obtaining the dihydro derivative.



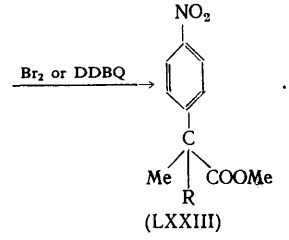
Monocyclic arenes do not react under these conditions.[308]

Such reactive organosilicon compounds as silylenol ethers and silyl ketene acetals and also *C*-silylated methyl acetate react successfully with mononitroarenes in the presence of F ion.[309,310] The salt *tris*-(dimethylamino)sulphonium difluorotrimethylsiliconate $(Et_2N)_3S^+Me_3SiF_2^-$, which is soluble in organic solvents, served as the source of F ion. The yields of products were reduced on using Bu_4NF.[310]

Adducts of 1,4- and 1,6-addition of $RSiMe_3$ were established in the reaction by PMR spectroscopy at –60 °C. Thus ketenacetal (LXXI) gives adduct (LXXII) with nitrobenzene.[310]

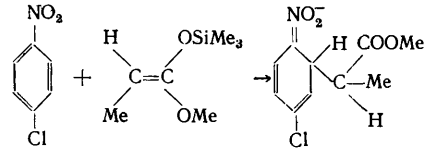


(LXXII)



(LXXIII)

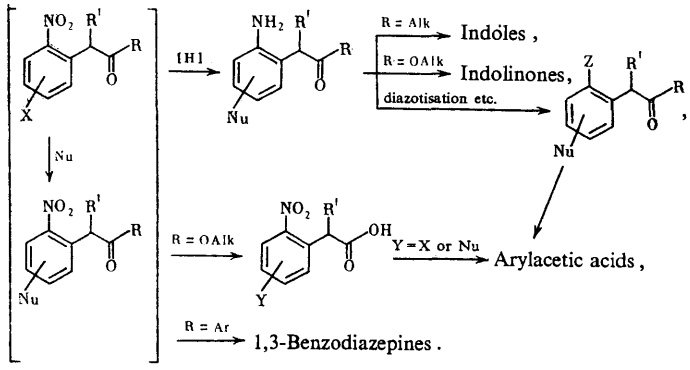
Adduct (LXXV) was established in the reaction of ketenacetal (LXXIV) with 4-chloronitrobenzene.[310]



(LXXIV) (LXXV)

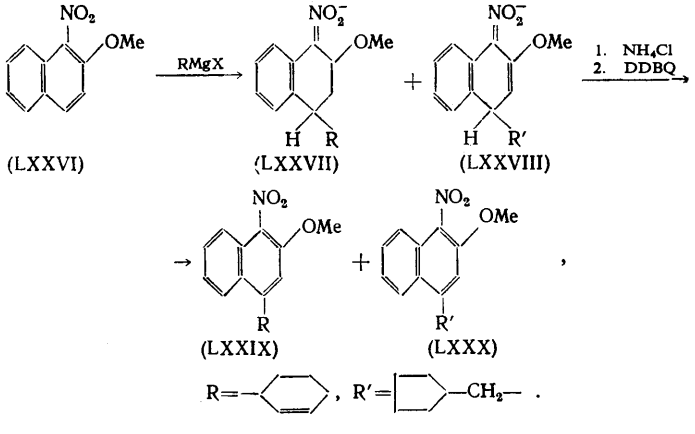
It was noted that alkali metal enolates did not add to nitroarenes under these conditions.[310]

The use of silyl ketene acetals, silylenol ethers and trimethylsilylacetic ester enables synthesis of α-nitroarylated ketones and ethers which are proposed for use in the synthesis of indoles, indolinones and arylacetic acids with various substituents.[311]

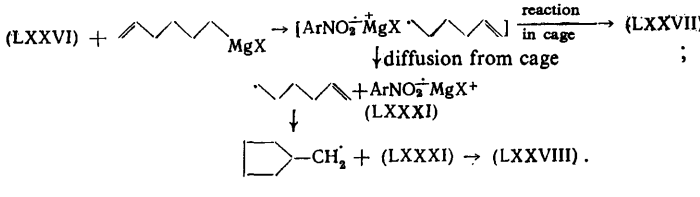


The principles discovered when studying the reaction of nitroarenes with Grignard reagents[288] and $RSiMe_3$ [309,310] are extremely complex. The regiochemistry of the addition is controlled by the size of the organosilicon compound. For example compound (LXXIII) is a single isomer in the reaction shown above. With less sterically hindered silyl ketene acetals such as Me_3SiCH_3COOMe the *ortho*-isomer is formed predominantly. In reactions of nitroarenes with $RSiMe_3$, as in reactions with RMgX, the halogen atom in the nucleus is not affected.[288,310] In the case of arenes with bi- and tricyclic nuclei it is possible to isolate the corresponding dihydro derivatives by treatment of the reaction mixture with acid. On oxidising the adducts with bromine dihydro compounds like (LXIX), which have a bromine atom in the nucleus, were detected.[310]

It is well known that the formation of anion radicals (AR) is repeatedly observed in reactions of nitroarenes with $RMgX$[284] or carbanions.[312] Furthermore, certain carbanions such as diphenylacetonitrile,[54] diphenylallyl,[313] fluorenyl[314,315] and others are oxidised by nitrobenzene to dimers, i.e. under definite conditions the reaction of $ArNO_2$ with RM may proceed by a single-electron-transfer (*SET*) mechanism. The problem then arises as to whether adducts (LVIII) and (LIX) are formed by the usual heterolytic route or by *SET*. The reaction of 2-methoxy-1-nitronaphthalene with hexen-5-ylmagnesium bromide was selected as a test for the existence of the *SET* mechanism.[288,291] [It is known that the hexen-5-yl radical rapidly cyclises at room temperature into the cyclopentylmethyl radical ($K \sim 10^5$ sec^{-1})[316]]. After adding DDBQ to the reaction mixture two alkylnitro compounds (LXXIX) and (LXXX) were isolated in the ratio 64:36 (overall yield 78%).



This result afforded the conclusion[288,291] that the reaction proceeded according to the radical route by at least 36%, but it is quite probable that the whole process is radical.

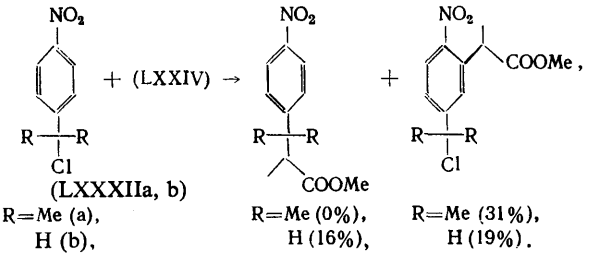


The order of reactivities of various RMgX [in reactions with nitroarene (LXXVI)] also supports the radical mechanism.

$$\text{iso-PrMgBr} > PhCH_2MgBr \simeq EtMgBr > MeMgBr.$$

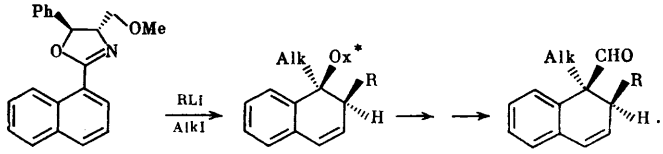
The order is determined by the ease of oxidation.[291,317]

Certain authors[310] considered the reaction of NO_2Ar with organosilicon compounds to be a heterolytic process. Their reasoning was as follows. Firstly, halogen on the nucleus is not affected in these reactions, if AR are formed then elimination of halogen must be observed. Secondly, in the reaction of (LXXIV) with 4-nitrocumyl chloride (LXXXIIa) replacement of chlorine did not occur and dicumyl or the dimer of the enolate were not detected.



However, replacement of chlorine takes place in the case of the unhindered *n*-$NO_2C_6H_4CH_2Cl$ (LXXXIIb). In addition 1-cyclopropyl-4-nitrobenzene reacts with (LXXIV) without fission of the cyclopropane ring. Finally, as already mentioned above, the formation of adducts (LXXII) and (LXXV) was detected by PMR spectroscopy and at –60 °C the signals in the PMR spectra were not broadened.[310]

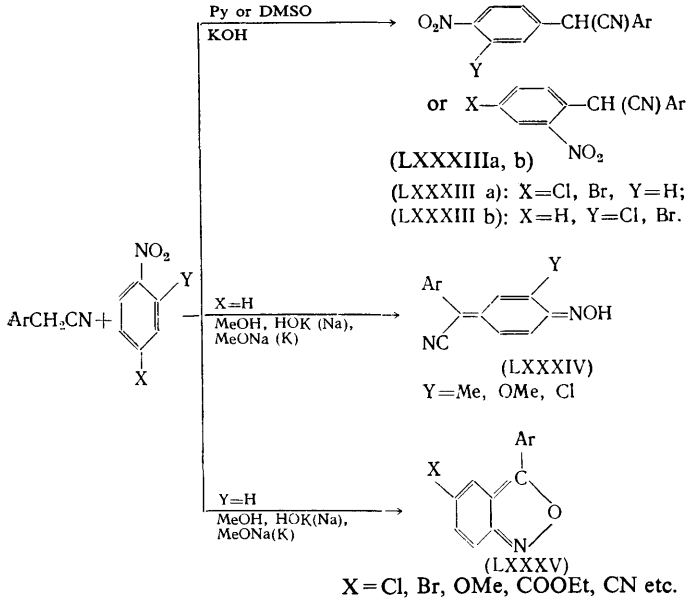
Usually the alkylation reactions described above are possible only for nitroarenes, the presence of such substituents as CF_3, CN or COR proved to be insufficient to activate the arene. However it was found comparatively recently that similar reactions (with RLi or RMgX) also occur on activation of the arene nucleus with an oxazoline group (see also p. 754). Products of *trans*-addition were formed in high yield on treating the adducts obtained with various electrophiles.[318–321]



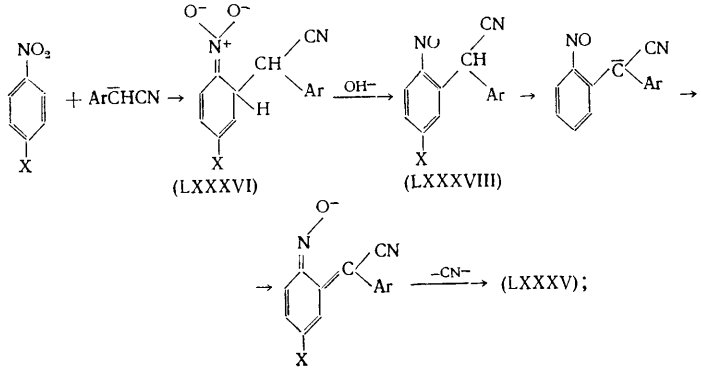
Such 'tandem addition' of RLi, RMgX and carbon-containing electrophiles has been described for (1-naphthyl)- and (2-naphthyl)-oxazolines.[318,319] Various proton sources were also used as electrophiles.[319–321]

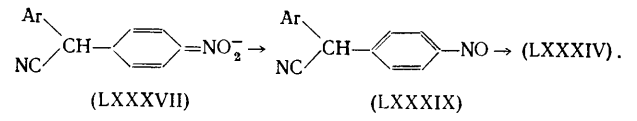
Adducts formed by addition of carbanions to nitro compounds (LVIII) and (LIX) are capable in certain cases of further spontaneous conversion which may be considered as oxidation-reduction processes with the participation of the NO_2 group. Thus over many years the steady attention of investigators has been attracted by the reaction of phenylacetonitrile and its substituted derivatives with nitroarenes which occasionally leads to the formation of unusual products.[54,322–333] The interaction of $ArCH_2CN$ with halonitrobenzenes may proceed according to three

different routes depending on the nature of the nitrocompound and the solvent.[54,322–333]



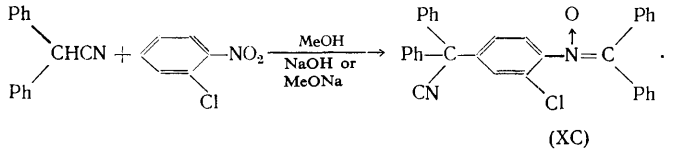
As already mentioned, replacement of halogen was observed in aprotic dipolar solvents like DMSO or Py.[54,322,323] However the situation changes sharply on replacing an aprotic solvent by methanol. In this case derivatives of quinonoxime (LXXXIV) (the oxime of 4-α-cyanoarylidene-2,5-cyclohexadien-1-one) are formed if the *para* position in the nitroarene is free.[324–328] This reaction route is effected with the selfsame variety of acetonitrile derivatives (Ar is homo- or heteroaryl) and various nitroarenes, including bicyclic and heterocyclic. When the *para* position is blocked and the *ortho* position free 3-arylanthranils (LXXXV) are formed which are used for the synthesis of 9-acridinone, acridine, benzophenones and 1,4-benzodiazepines.[323,329–331,334] The formation of both compounds (LXXXIV) and (LXXXV) may be explained within the framework of one or the other mechanism, comprising attack of the carbanion at the *ortho* or *para* position of the benzene ring [formation of adducts (LXXXVI) and (LXXXVII)], elimination of hydroxyl ion which leads to nitroso compounds (LXXXVIII) and (LXXXIX), intramolecular cyclisation of *o*-nitro compound (LXXXVIII) to anthranil (LXXXV) or isomerisation of the *p*-nitro compound (LXXXIX) to quinonoxime (LXXXIV).[54,323,325]



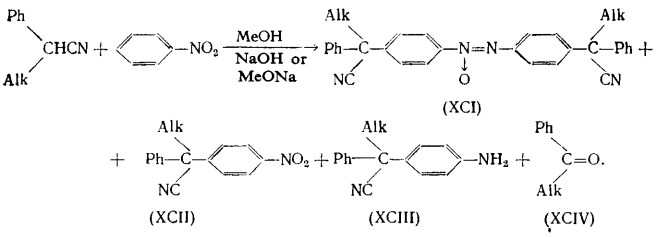


Regrettably it is still unclear in what way the conversion of (LXXXVI) →(LXXXVIII) or (LXXXVII)→(LXXXIX) occurs. The strong influence of solvent on the route of reaction is also not understood.

Phenylacetonitriles substituted in the α-position are evidently unable to give products like (LXXXIV) and (LXXXV). Diphenylacetonitrile forms nitrone (XC) in high yield on reaction with a nitroarene with a free *para* position in the benzene ring.[54,323,332–334]



Under these conditions α-alkylphenylacetonitriles gives a complex mixture of compounds (XCI)–(XCIV) with $PhNO_2$ among which is the product of replacement of hydride ion.[54,332]



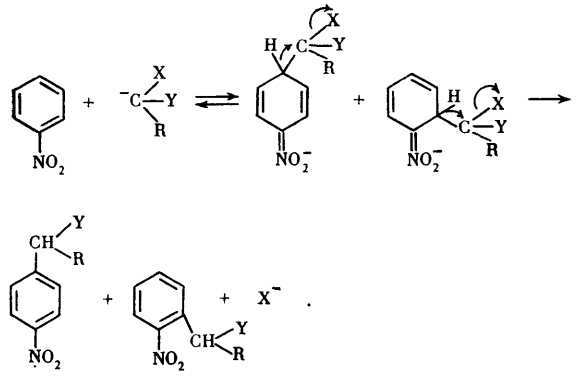
The presence of amine (XCIII) in the reaction mixture probably indicates that 1 mole of nitro compound behaves as an oxidising agent in relation to an adduct like (LXXXVII). The formation of all the remaining products is readily explained by subsequent conversions of nitroso compounds.[54,332,333] It is noted that in weakly polar solvents like benzene the anion of diphenylacetonitrile is oxidised by nitroarenes to the dimer.[54,332]

2. Vicarious nucleophilic substitution of hydrogen

The alkylation of nitroaromatic compounds by carbanions has been described above. In these reactions removal of hydride ion from the intermediate complex is effected by an oxidising agent. The oxidising agent is introduced into the reaction mixture specially or the initial nitroarene fulfils this role, in this way an intra- or intermolecular oxidation of the σ-complex occurs.

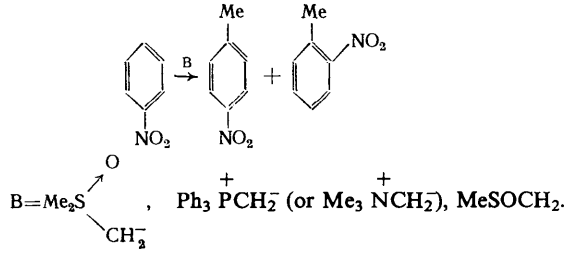
Another route for converting adducts (LVIII) and (LIX) into alkylnitroarenes has emerged using carbanions containing 'good' leaving groups. The essence of the reaction is that under the action of the carbanion a hydrogen atom in the position *ortho* or *para* to the nitro group of the nitroarene is replaced. The substituent X acts as a 'vicarious' leaving group and Makosza and collaborators

have proposed the general name of vicarious nucleophilic substitution (VNS) for the whole process.[335–339]

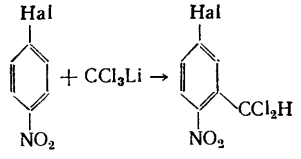


X is a leaving group: Cl, Br, PhS, PhO, $R_2NC(S)S$, etc.; Y is a group stabilising the carbanion: SO_2Ar, SO_2NR_2, SO_2OR, SOAr, CN, COOR, $CONR_2$, $P(O)Ph_2$, $P(O)(OEt)_2$, etc.; R = H, Alk, Ar. In spite of the fact that individual examples of similar reactions were known previously,[340–346] only the systematic work of Makosza and collaborators has attracted general attention to like reactions and the study of them has proceeded independently.

It is known that methylation of nitrobenzene and certain of its substituted derivatives occurs under the action of methylids of sulphur, phosphorus or of dimethylsulphinyl carbanion.[340,341]



The reaction of halonitrobenzenes with CCl_3Li, which may serve as a method of dichloromethylating and formylating nitroarenes, should also be considered as a VNS.[342,347]

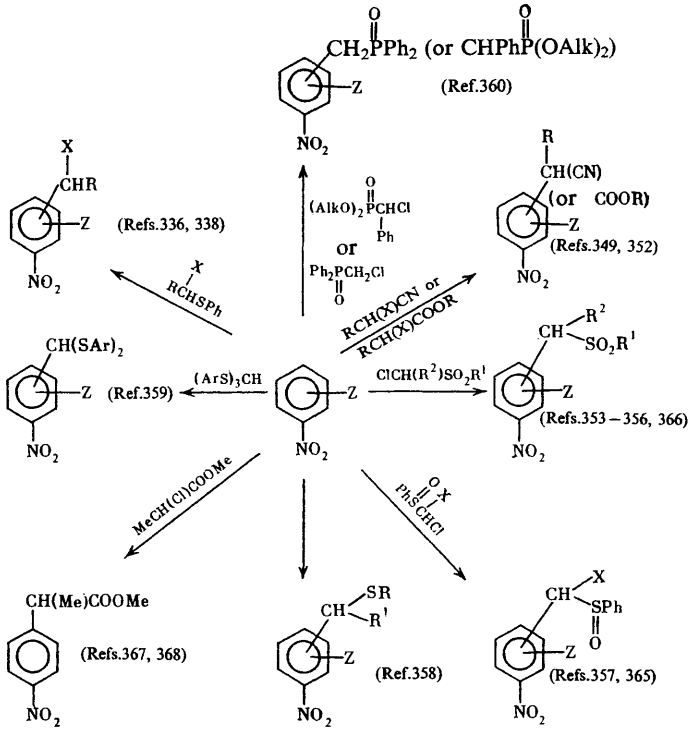


The possibility of nucleophilic substitution of hydrogen in nitroheteroarenes has been shown.[343–346]

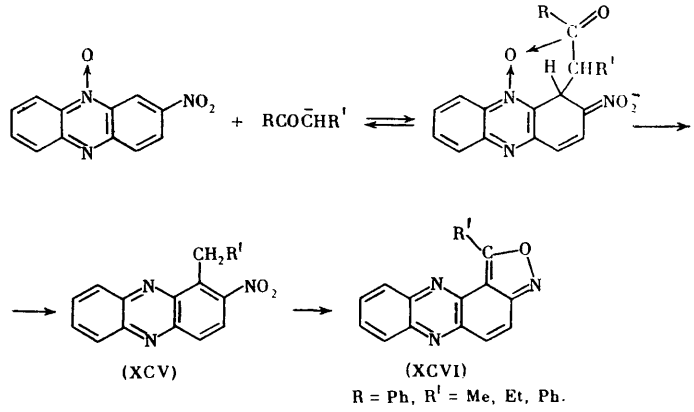
In the general case, as shown by Makosza and collaborators,[336–339] for the successful achievement of the VNS reaction, it is necessary that the carbanions are sufficiently stable and do not react with the CH-acids from which they were formed. This is attained by an appropriate combination of groups X and Y. However when X = Hal not many CH-acids satisfy this requirement consequently CH-acids are used which contain poorer leaving groups such as PhS, PhO, $R_2NC(S)S$, etc.[336–339]

The choice of base and solvent is another important requirement. Such systems as NaOH(KOH)/DMSO or NH_3, NaOH/DMF, R_4NOH/PhH(PhCl) proved to be most suitable. This means that solvent-separated ion pairs or free ions possess the greatest reactivity. Under such conditions the VNS reaction enables the introduction of various α-functionalised alkyl groups into the *ortho* and *para* positions of nitro aromatic compounds.[335–368] It should be mentioned that the products of VNS contain at least one acid hydrogen atom in the α-position, consequently they may react with other electrophiles such as RHal, RCHO, etc. (Scheme 3).[347]

Scheme 3



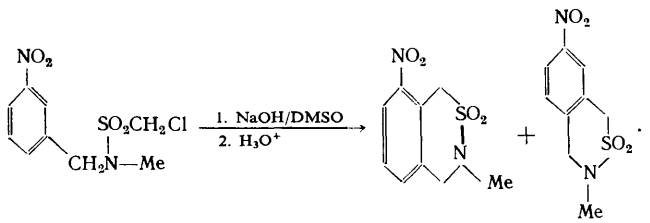
A more complex case of the VNS reaction has been described[346] in which the leaving group is carboxylate ($RCOO^-$). Various products are obtained depending on the nature of the ketone which reacts with 2-nitrophenazine-10-*N*-oxide. These include the normal products of substitution of hydride ion (XCV), anthranils (XCVI) and other more complex compounds (see previous section).[346]



(XCV) (XCVI)

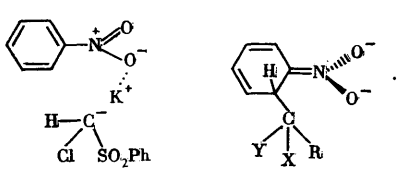
R = Ph, R' = Me, Et, Ph.

The intramolecular VNS process may serve as a source of various isocyclic and heterocyclic compounds.[369]

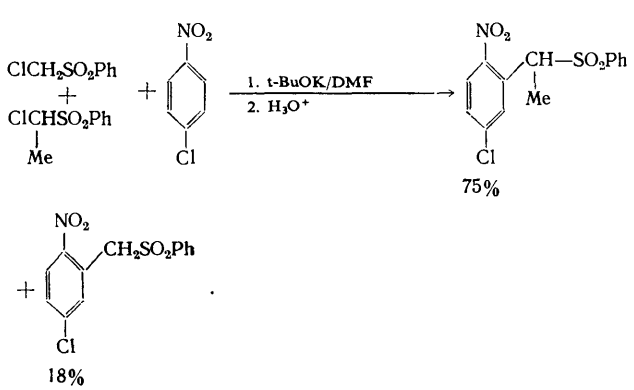


The intramolecular VNS reaction is used for the synthesis of tetracycline derivatives.[370]

The VNS reaction is distinguished by several special features. Tertiary carbanions usually replace a hydrogen atom in the *para* position of the nitroarene,[337,338,357] although there are several exceptions.[349,357] A mixture of *ortho* and *para* isomers, the ratio of which depends on the size of groups X and Y, is formed from secondary carbanions when using DMSO, DMF or liquid NH_3 as solvent.[349,350] On the other hand, the application of the THF/t-BuOK system enables selective replacement of hydrogen in the *ortho* position to the nitro group.[351,352,356] This is explained by the fact that the carbanions are mainly in the form of contact ion pairs or aggregates with the potassium ion in THF in difference to DMSO. The potassium cation, forming a bond with negatively charged oxygen in the NO_2 group, directs the associated carbanion to the *ortho* position.[352,356]



However under definite conditions (DMF, t-BuOK, –40 to –30 °C)¶ tertiary carbanions like α-chloroalkylphenylsulphone also readily substitute hydrogen in the *ortho* position of a nitroarene. Furthermore in competing reactions of tertiary and secondary carbanions the former react at the higher rate.[366]



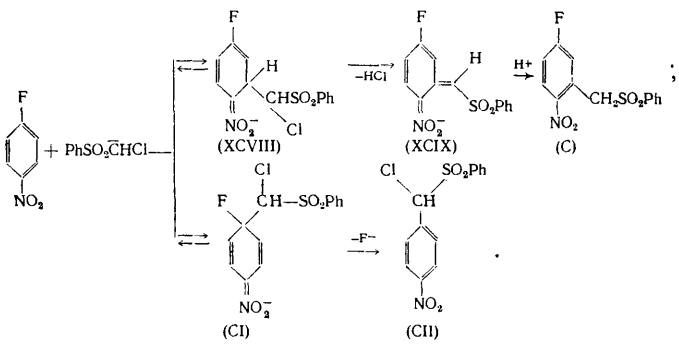
¶Tertiary carbanions and *o*-nitrobenzyl carbanions of the corresponding products are unstable at higher temperatures.[367]

Of the two possible *ortho* isomers the most hindered (1,2,3 isomer) is formed for the majority of 3-substituted nitrobenzenes.[353,356] This same special feature of the reaction was also observed in the methylation of nitroarenes by ylids.[342] Thus by changing the solvent and by varying groups R, X and Y in the carbanion it is possible to change the regioselectivity of the VNS reaction in an effective manner.

The VNS reaction is distinguished by its special features for naphthalenes.[365] 1-Nitronaphthalene gives a mixture of 2- and 4-substituted products [in reactions with $ClCH(R^2)SO_2R^1$ the ratio of 2-isomer : 4-isomer = 10 : 1]. The preference for attack by the carbanion at position 2 is comprehensible on considering the mesomeric structures of the appropriate σ-adducts. Reaction of 2-nitronaphthalene with secondary carbanions occurs exclusively at position 1. This tendency was so large that no VNS reaction occurred on blocking position 1 with a MeO group but a nucleophilic aromatic substitution of the MeO group took place. No reaction occurred with tertiary carbanions (such as α-chloropropyl-p-tolylsulphone).[365]

Donor groups (NMe_2, Me, OR) and even negatively charged groups of the COO^- type proved to have no significant influence on the VNS reaction.[355,361] Mononitrophenoxides did not undergo a VNS reaction, however this reaction is possible for di- and trinitrophenoxides.[362] In this case it probably occurs as a nucleophilic addition to the cyclohexadienenitronate system.[362] We also note that VNS reactions are known for DNB and TNB in which it is possible to substitute two and three hydrogen atoms respectively.[362]

Like the reactions with RLi, RMgX or $RSiMe_3$ vicarious nucleophilic substitution may be used for alkylating halogen-substituted nitrobenzenes since the rate of substituting hydrogen is far greater than that for Cl, Br or I. Replacement of both hydrogen and fluorine or nitro group depending on the conditions was observed in *o*- and *p*-fluoronitrobenzenes and *p*-dinitrobenzene.[336–339,363,368] An interesting dependence of reaction route on base concentration has been discovered.[363] On interacting *p*-fluoronitrobenzene with chloromethylphenylsulphone (XCVII) at a ratio (XCVII)/t-BuOK = 2 the formation of both possible products (C) and (CII) was observed but with a four fold excess of t-BuOK the product of VNS (C) was obtained exclusively.



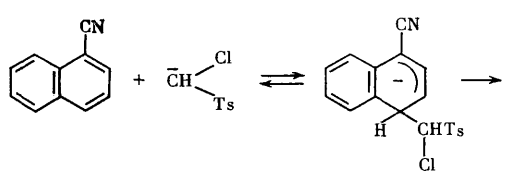
This dependence is displayed even more clearly in the competing reaction of phenoxyphenylacetonitrile (CV) with a mixture of NO_2Ph and n-$FC_6H_4NO_2$. At a ratio (CV)/t-BuOK equal to 2 approximately identical amounts of the VNS product and that from fluoride

ion substitution were obtained. At a ratio (CV)/t-BuOK = 4 practically only the product of hydrogen substitution was obtained. From this it follows that addition of carbanion to an unsubstituted carbon atom [adduct (XCVIII)] occurs more rapidly than formation of an adduct containing a fluorine atom at the geminal node (CI).[339,363]

It is certain that the VNS reaction includes the reversible formation of an intermediate σ-complex. It is assumed that its conversion into the reaction product may occur either by removal of the leaving group X from the carbanion with a simultaneous 1,2-hydride shift or by base catalysed elimination of HX.[336–339,363] The observed dependence of the reaction route on base concentration and also isotope effects K_H/K_D found in several cases,[339,363,368] indicate that the second mechanism is true. The mechanism of VNS therefore includes a rapid, reversible σ-complex formation and subsequent slow elimination of HX. The rate of elimination must, nonetheless, be more than the rate of addition of carbanion to the carbon bonded to halogen.[339]

Regarding the mechanism of formation of the σ-complex, the authors regard this reaction to be ionic.[339] The clearly expressed influence of solvation of the cation on the route of addition of carbanion to NO_2Ar indicates this. In addition cyclisation products were not detected in the reaction of 1-chloro-5-hexenylphenylsulphone with nitroarenes[339] (cf. addition reactions of RMgX to NO_2Ar[285]).

In conclusion we note that the VNS reaction, like the alkylation reaction described in Chapter IV, Section 1, is only possible for nitroaromatic compounds. Arenes with less strongly electron-accepting substituents in the nucleus, as a rule, do not take part in this reaction. The reaction of 1-cyanonaphthalene with chloromethyl-4-tolylsulphone leading to *bis*-cyclopropane derivative (CIV) proved to be even more unexpected.[364]



(CIII) (CIV)

This result is probably explained by addition of carbanion at the C-4 atom with subsequent intramolecular nucleophilic substitution which leads to the monoannulated product (CIII). The latter, being an active Michael acceptor, adds a second molecule of carbanion finally forming (CIV).[364]

We note that vicarious nucleophilic substitution has been illuminated in more detail in a review.[371]

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Thermal reactions of thiyl radicals

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ABSTRACT. The review presents data on the methods of generation and properties of thiyl radicals. The results of studies on the reactivities of thiyl radicals in thermal processes, permitting the synthesis of a wide variety of organic sulphur compounds and compounds of other types, are surveyed.

The bibliography includes 167 references.

Contents

I. Introduction 778
II. Generation, detection, structure, and properties of thiyl radicals 778
III. High-temperature reactions of thiyl radicals 781
IV. Liquid-phase thermal reactions of thiyl radicals 785
V. Reactions of hydrogen sulphide, thiols, and dialkyl sulphides and polysulphides with halogenoalkenes 786
VI. Thermal synthesis of thiophen and its derivatives and analogues 788
VII. Conclusion 789

I. Introduction

Thiyl (sulphur-centred) free radicals are short-lived reactive sulphur-containing intermediates RS$^{\cdot}$ (R = H or an organic group) whose sulphur atom has an unpaired electron. They participate in many chemical reactions, including various industrial and natural processes and are therefore of practical and theoretical interest.

The stability of free radicals is determined by the degree of delocalisation of the unpaired electron.[1] This can be estimated quantitatively from electronic, spectroscopic, and EPR data. According to Walter's classification, free radicals can be divided into two groups:[2]

1. The radical centre possesses an unshared electron pair together with the unpaired electron. The delocalisation of the electron is promoted by electron-donating substituents at the radical centre.

2. The paramagnetic centre has only the unpaired electron whose delocalisation is promoted by both electron-donating and electron-accepting substituents.

The energy characteristics of the level occupied by the unpaired electron have also been used recently for the classification of free radicals. According to this classification, the radicals can be divided into three groups:[3]

1. Electrophilic radicals containing the unpaired electron in the highest bonding orbital. Such radicals tend to be converted into the energetically more favourable ionic state by capturing an electron.

2. Nucleophilic radicals containing the unpaired electron in the lowest antibonding orbital and exhibiting a tendency to give it up.

3. Amphoteric radicals containing the unpaired electron in a non-bonding orbital.

Thiyl radicals having an unshared electron pair at the radical centre are electrophiles judging from their reactivity. The energies of the highest molecular orbitals occupied by one electron may serve as a characteristic of the relative stability of thiyl radicals.[3]

This review deals for the first time with thermal methods for the generation of thiyl radicals from very simple sources such as hydrogen sulphide and its organic derivatives† as well as the methods for high-temperature organic synthesis using thiyl radicals. The description of these data (mainly obtained by the present authors) is preceded by an account of the general information about the method of generation and detection and the properties of thiyl radicals secured earlier in the study of the photochemical and other types of reactions and frequently quoted in certain reviews and monographs.

II. Generation, detection, structure, and properties of thiyl radicals

1. Generation

Thiyl radicals usually arise in the photolysis, radiolysis, and thermolysis of hydrogen sulphide and its organic derivatives (thiols, sulphides, thionitrites, etc.). They can also be generated on treatment of the above compounds by initiators such as peroxides, diazo-compounds, etc.[6,7] Overall, the dissociation energies of the S–H, S–C, and S–S bonds are fairly high (87, 69, and 63 kcal mol^{-1} respectively) compared with the dissociation energies of other bonds (N–N, O–O, Si–Si, Ge–Ge, Sn–Sn, As–H, Sn–H, Sn–C, etc.) (Table 1).

The strength of the E–H, and E–C bonds involving elements of a given Group of the Periodic System decreases with increase in the atomic number of the element E (Table 1). Accordingly the S–H, and S–C bonds are weaker than the O–H and O–C bonds but are more stable than the Se–H and Se–C bonds respectively. The S–H bonds in alkanethiols are stronger than the CH_2–H bonds in propylene and toluene but weaker than the O–H bond in alkanols.[8]

The strength of the bonds between two identical non-metal atoms or two atoms of an amphoteric non-transition metal (E–E) in Group IV decreases with increase in the atomic number of the element E. On the other hand, the energy of the E–E bonds

†As regards the role of thiyl radicals in reactions of organic compounds with participation of elemental sulphur, see Voronkov, et al.[4,5]

involving Group V–VII elements in the Third Period (P–P, S–S, and Cl–Cl) proves to be a maximum in the given Group, which can apparently be accounted for by the $p-\pi$, $d-\pi$ interaction, as a result of which the effect of the repulsion of the unshared electron pairs loses its importance. By virtue of this, the S–S bond in organic disulphides is much stronger than the O–O, Se–Se, and Te–Te bonds in the isostructural peroxides, diselenides, and ditellurides (Table 1).

Table 1. The average enthalpies of the E–H, E–C, and E–E bonds involving non-metallic elements.

Element E	ΔH°_{298}, kcal mol^{-1}*		
	E–H	E–C	E–E
C	99	83 (76)	83 (76)
Si	76	76	46 (42)
Ge	69	57	38
Sn	60	46	39
N	89 (93)	73	21 (27)
P	77 (63)	63	51
As	47	55	43
O	105 (110)	80 (85)	45
S	87	69	63
Se	75	60	48
Te	63	48	36
F	134	116	38
Cl	102	76	58
Br	86	63	46
I	71	43	36

Note. The data were taken from handbooks: V I Vedeneev, L V Gurvich, V N Kondriat'ev, et al. *Energii Razryva Khimicheskikh Svoiazei* (Chemical Bond Dissociation Energies), Izd. Akad. Nauk SSSR, Moscow, 1962, 215 pp; A J Gordon, R A Ford *A Chemist's Companion* (Translated into Russian), Izd. Mir, Moscow, 1976, p. 134

*The values determined by other methods are given in brackets.

The structure of the alkyl groups linked to the sulphur atom in alkanethiols, alkyl sulphides, and alkyl disulphides has little influence on the strength of the S–H, S–C, and S–S bonds. On the other hand, the presence of a π-electron system at the sulphur atom reduces the strength of these bonds[9,10] (Table 2).

The difference between the dissociation energies of the C=S and C–S bonds (45 kcal mol^{-1}) is much smaller than the difference between the dissociation energies of the C=O and C–O bonds (73 kcal mol^{-1}). The conversion of thiyl radicals into thiocarbonyl compounds is usually not observed, while the analogous reactions involving oxyl radicals, readily affording carbonyl compounds, do take place.

The steric hindrance in the reactions involving thiyl radicals is less significant than in the reactions involving oxyl radicals, since the C–S bond length (1.81 Å) is greater by almost 30% than the C–O interatomic distance (1.42 Å).[1]

The electron affinity of thiyl radicals is greater than that of oxyl radicals, which is apparently due to the presence of unoccupied *d* orbitals in the sulphur atom. The stabilisation of thiyl radicals at low temperatures is difficult, since, in contrast to oxyl radicals, they readily recombine (cf. the S–S and O–O bond energies listed in Table 1).

Table 2. The dissociation energies (E_D) of the S–H, C–S, and S–S bonds in certain organic sulphur compounds.[9,10,11]

Compound	E_D(S–H) kcal mol^{-1}	Compound	E_D(S–C), kcal mol^{-1}	Compound	E_D(S–S), kcal mol^{-1}
HS–H	92.0±1.0	HS–Me	75.0±1.5	HS–SH	66.0±2.0
MeS–H	92.0±1.5	HS–Et	72.0±1.5	MeS–SMe	74.0±2.0
EtS–H	92.0±2.0	HS–Pr	72.0±1.0	AlkS–SAlk	74.0±2.0
AlkS–H	92.0±2.0	HS–Pr-iso	71.0±1.5	FS–SF	61.0±4.0
PhS–H	82.0±1.5	HS–Bu-t	69.0±1.5	PhS–SH	61.0±1.5
CH_2=CHS–H	84.0±2.0	HS–CH_2CH=CH_2	54.3±1.0	PhS–SMe	65.0±1.5
HS_2–H	70.0±1.5	HS–CH=CH_2	83.0±3.0	PhS–SPh	55.0±1.5
$AlkS_2$–H	70.0±1.5	HS–Ph	86.0±2.0	HS_2–SH	50.0±2.0
HS_3–H	70.0±1.5	HS–CHO	74.0±2.0	HS_2–SMe	54.0±2.0
HS_{3+n}–H	70.0±1.5	HS–COMe	73.0±2.0	HS_2–SAlk	54.0±2.0
$AlkS_{3+n}$–H	70.0±1.5	MeS–Me	77.0±1.5	HS_2–SPh	44.0±2.0
		MeS–Et	74.0±1.5		
		AlkS–Me	77.0±1.5		
		MeS–CH_2Ph	59.4±2.0		
		PhS–Me	67.4±1.5		
		AlkS–Bu-n	71.0±1.5		
		MeS–Ph	89.2±2.0		
		MeS–CN	97.0±1.5		

The enthalpy of formation of the sulphydryl radical HS$^{\cdot}$ varies in the range 31.9–35.0 kcal mol^{-1} according to different data.[9,12–14] The dipole moments, obtained by the EPR method, are contradictory (0.62 D [15] or 1.47 D [16]). The ν(SH) and ν(SD) frequencies in the IR spectra of HS$^{\cdot}$ and DS$^{\cdot}$ radicals matrix-isolated in argon are respectively 2450.8 and 1847.8 cm^{-1}.[12] The ionisation potential of HS$^{\cdot}$ is 10.5 eV [12] and its electron affinity varies in the range from 53.1 kcal mol^{-1} at −273 °C to 58.8 kcal mol^{-1} at 1527 °C.[17]

The enthalpy of formation of alkanethiyl radicals decreases with increasing length and degree of branching of the alkane chain from 31 for $CH_3S^{\cdot}$ to 15 for n-$C_4H_9S^{\cdot}$ and 11 kcal mol^{-1} for t-$C_4H_9S^{\cdot}$.[4] The entropy and heat generating capacity increase in the same sequence.[18]

The simplest arenethiyl radical $C_6H_5S^{\cdot}$ is distinguished by a high enthalpy of formation (ΔH°_{298} = 56.8 ± 2.0 kcal mol^{-1}).[14] Its stabilisation energy (9.6 kcal mol^{-1}) is close to the stabilisation energy of the benzyl radical (13.5 kcal mol^{-1}), but is appreciably lower than that of the phenoxyl radical (17.5 kcal mol^{-1}).[14]

The molecular and electronic structures of the $CH_3S^{\cdot}$ and $C_2H_5S^{\cdot}$ radicals, which have the C_s symmetry, were calculated by the MNDO method. The molecular orbital is localised predominantly on the sulphur atom, is located at right angles to the C–S bond, and has the A' symmetry.[19] This agrees with experimental data characterising the Mo of thiyl radicals as π orbitals. The heats of the rearrangement reaction involving the migration of a hydrogen

atom in the $CH_3S^{\cdot}$ and $C_2H_5S^{\cdot}$ radicals have been calculated:

$$CH_3S^{\cdot} \rightarrow \dot{C}H_2SH \ (0.6 \text{ kJ mol}^{-1}),$$

$$CH_3CH_2S^{\cdot} \rightarrow CH_3\dot{C}HSH \ (26.4 \text{ kJ mol}^{-1}).$$

The values obtained indicate the exothermic character of these reactions.

The rearranged radicals $\dot{C}H_2SH$ and $CH_3\dot{C}HSH$ have the C_s symmetry, while the molecular orbital is located at right angles to the CSH plane and has the A'' symmetry.

2. Detection

In contrast to the alkoxyl radicals $RO^{\cdot}$, the alkanethiyl radicals $RS^{\cdot}$ cannot be detected in the liquid phase by the EPR method since their $p-\pi$ orbitals are degenerate and the spin–orbital interaction constants for the sulphur atom are large.[20,21] The EPR spectra of alkanethiyl radicals in the solid state have a fairly anisotropic g-tensor,[22–24] whose components can differ appreciably depending on the structure of the radical.[25] In the thiyl radicals where the sulphur atom is linked to a π-electron system ($CH_2=CH$, C_6H_5, etc.), the degeneracy of the π levels is removed as a result of the delocalisation of the unpaired electron over the multiple bond. Their EPR spectra can be recorded in certain cases even in liquid media. The photochemically generated 2,4,6-tri-(t-butyl)benzenethiyl radical gives in its EPR spectrum a singlet ($\Delta\beta$ = 2.89) with g = 2.0103 and an unresolved hyperfine structure due to the hydrogen atoms.[26] This radical is in equilibrium with the dimer below 313 K (ΔH = –23.3 kcal mol^{-1}). After prolonged photolysis of thiophenols, a very complex effect of the chemically induced dynamic electronic polarisation (CIDEP), which promotes a marked decrease of the signal, was observed. In many cases, after the removal of the source of irradiation, the height of the lines in the EPR spectra of thiyl radicals increases suddenly and then slowly diminishes.[27]

A strong signal with a typically anisotropic g-factor was detected in the EPR spectrum of diphenyl disulphide irradiated with UV light at –200 °C.[28] The g-tensor is almost axially symmetrical and has the extremum values g = 2.006 and 2.012. The marked anisotropy of the g-factor is caused by the localisation of the unpaired electron on the sulphur atom of the $C_6H_5S^{\cdot}$ radical.[28,29] The absorption spectrum of $C_6H_5S^{\cdot}$ contains bands of 355 and 380 nm, while the luminescence spectrum has bands at 374 and 240 nm.[30] The colour of the 4-dimethylaminobenzenethiyl and 4-diphenylaminobenzenethiyl radicals is appreciable even at –73 °C.[29]

Thiyl radicals have also been identified by EPR spectroscopy in the form of their spin-adducts with different trapping agents. The spin-adducts of thiyl radicals with nitroso-compounds are unstable and are therefore detected only when they are generated directly in the resonator of the spectrometer.[31,32]

Thiyl radicals have been detected as spin-adducts with 2-nitrosopropane, 2-methyl-2-nitrosopropane, nitrosobenzene, pentamethylnitrosobenzene, nitrosodurene, 2, 4, 6-tri-(t-butyl)nitrosobenzene, and 5,5-dimethyl-Δ^1-pyrroline N-oxide.[33–37]

Thiyl radicals react at a high rate with stable radicals. The rate constants for the reactions between *para*-substituted benzenethiyl radicals and free radicals such as di(t-butyl)nitroxyl (DBNO$^{\cdot}$) and galvinoxyl (Q$^{\cdot}$) have been determined.[37] In the case of Q$^{\cdot}$ (ρ^+ = +0.25), the reaction is controlled solely by the stability of the thiyl radical, while for DBNO$^{\cdot}$ the polarity of the transition state (ρ^+ = +0.75) is also important.

The radical $C_6H_5S^{\cdot}$ reacts at a higher rate with pentamethylnitrosobenzene than with 2-methyl-2-nitrosopropane or nitrosodurene.[38]

The EPR spectra of the spin-adducts of the thiyl radicals with 2-methyl-2-nitrosopropane consist of a triplet with similar values of the g-factor and a_N constants in the range 16.5–18.5 G, whose values are characteristic solely of thiyl radicals.[20,21,39–42]

A specific feature of these spin-adducts is the rapid disappearance of the signal when irradiation ceases.[43] The g-factor of thiylalkyl(thiylaryl)nitroxyls is greater than the g-factor for the free electron.[40] The temperature and the solvent do not affect the parameters of the EPR spectra of thiylnitroxyls.

3. Chemical properties

The characteristic reactions of thiyl radicals involve addition to multiple bonds and the abstraction of a hydrogen atom from organic molecules. The rates of these processes depend on polar effects as a consequence of the high electron affinity of thiyl radicals and the strength of the S–H bond arising when they are generated. In reactions involving the abstraction of a hydrogen atom from hydrocarbons, thiyl radicals are more selective than the bromine atom or the trichloromethyl radical.[44]

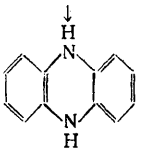
Thiyl radicals function as agents transferring hydrogen atoms from molecules to radicals.:[45]

$$RS^{\cdot} + HR' \rightleftarrows RSH + {}^{\cdot}R'. \quad (1)$$

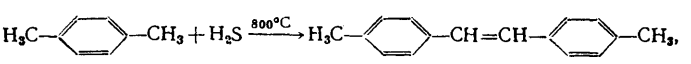
Reaction (1) is sensitive to steric hindrance in molecules and radicals. As a result of the transfer of a hydrogen atom, thiyl radicals accelerate the pyrolysis of hydrocarbons or even alter its direction[8,46–52] and they catalyse the decarbonylation of aldehydes[53] and the conversion of a series of alcohols into ketones.[54] At temperatures above 450 °C in hydrogen sulphide, the thermal conversions of aniline into 5,10-dihydrophenazine,[55] of benzaldehyde into stilbene,[56] of *p*-xylene into 4,4′-dimethylstilbene,[57] and of hexachlorocyclopentadiene into hexachlorobenzene[58] are initiated.

Hydrogen sulphide accelerates with thermal dehydrodimerisation of thiophen into isomeric bithienyls[59] [reaction (6)]:

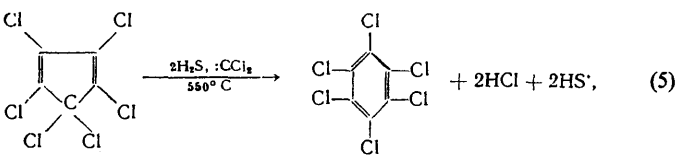
$$C_6H_5NH_2 + HS^{\cdot} \xrightarrow{750^\circ C} C_6H_5\dot{N}H + H_2S, \quad (2)$$



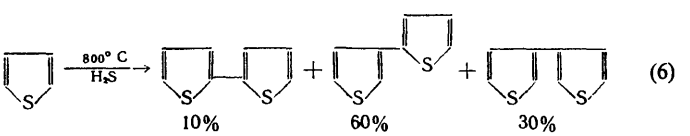
$$2C_6H_5CHO + 2H_2S \xrightarrow{500^\circ C} C_6H_5CH{=}CHC_6H_5 + 2H_2O + 2S, \quad (3)$$



(4)



(5)



(6)

In a hydrogen sulphide atmosphere, ethyl vinyl ether is transformed, with a high degree of conversion, preferentially into s-butyl vinyl ether. The interaction with hydrogen sulphide over iron sulphide leads to the almost complete conversion of ethyl vinyl ether into acetaldehyde diethylacetal:[60]

$$CH_2{=}CHOCH_2CH_3 \xrightarrow{Z} \underset{(A)}{CH_3CH(OC_2H_5)_2} + \underset{(B)}{CH_2{=}CHOCH(CH_3)C_2H_5}.$$

Reagent Z	N_2	H_2S	H_2S over FeS
Yield of (A), %	8.5	7.0	90
Yield of (B), %	8.5	64.0	—

In the hydrogen sulphide–iodine system, the decomposition of alkyl vinyl ethers at 250 °C leads to trithioacetaldehyde and ethanol.[61] The catalytic effect of iodine apparently consists in the initiation of the formation of thiyl radicals[62] [reaction (7)] which subsequently substitute the RO group in the ether via reaction (8):

$$I_2 \rightleftarrows 2I^{\cdot}; \quad I^{\cdot} + H_2S \rightleftarrows HI + HS^{\cdot}, \tag{7}$$

$$CH_2{=}CHOR + HS^{\cdot} \rightarrow CH_2{=}CHSH + {}^{\cdot}OR,$$

$$CH_2{=}CHSH \rightarrow CH_3CHS \rightarrow {}^1/_3(CH_3CHS)_3,$$

$$RO^{\cdot} + H_2S \rightarrow ROH + HS^{\cdot},$$

$$R = C_2H_5, \quad n\text{-}C_4H_9. \tag{8}$$

The chemical properties of thiyl radicals are reflected most clearly by their reactions with unsaturated compounds. The free-radical addition of hydrogen sulphide and thiols to multiple bonds (the thiylation reaction) is usually initiated by peroxides, azo-compounds, and also by radiation and UV irradiation.[7, 63–78] These reactions confirm the electrophilic nature of thiyl radicals, since they attack the reaction centre with the highest electron density. The mechanism of the thiylation reaction is described by the following general scheme:

$$RSH \rightarrow RS^{\cdot} + H^{\cdot}, \tag{9}$$

$$RS^{\cdot} + \rangle C{=}C\langle \rightleftarrows RS{-}\overset{|}{C}{-}\overset{|}{\underset{\cdot}{C}}\langle, \tag{10}$$

$$RS{-}\overset{|}{C}{-}\overset{|}{\underset{\cdot}{C}}\langle + HSR \rightleftarrows RS{-}\overset{|}{C}{-}\overset{|}{C}{-}H + RS^{\cdot}. \tag{11}$$

Reactions (9)–(11) cannot be achieved with thermal initiation apparently because of the low thermal stability of the sulphides formed, which promotes the reversibility of the process.[79] Reactions (10) and (11) are appreciably exothermic, which leads to rapid chain propagation.

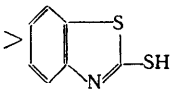
The stability of the radicals RS$^{\cdot}$ exerts the greatest influence on the rate of homolytic thiylation. The radicals are stabilised by electron-donating substituents and are destabilised by electron-accepting ones.[80] The rate of abstraction of the hydrogen atom from the HS group in alkanethiols diminishes approximately by a factor of 20 in the following sequence based on different alkyl groups:[45,81–83]

$$C_5H_{11} > C_4H_9 > (CH_3)_2CHCH_2 > (CH_3)_3C.$$

The sulphydryl hydrogen atom is abstracted from thiophenol several hundred times more readily than from butanethiol.[84]

The ability of thiols to generate thiyl radicals has been estimated quantitatively from the rate of their oxidation, which decreases in the following sequence:[85,86]

$$ArSH > C_6H_5CH_2SH > HOCOCH_2SH > RCH_2SH >$$

$$> RR'CHSH > RR'R''CSH > \text{  }$$

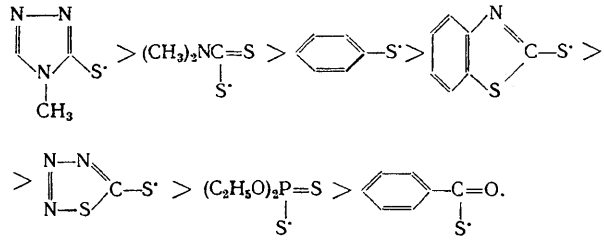
In reactions involving addition to a double bond, the reactivity of the radicals RS$^{\cdot}$ diminishes in the following sequence of substituents R:[84]

$$Cl_3CCO > Cl_2CHCO > ClCH_2CO > CH_3CO > C_6H_5 > HCOCH_2.$$

The rate of addition of arenethiyl radicals 4-$XC_6H_5S^{\cdot}$ to vinyl monomers is inversely proportional to the electron-donating properties of the *para*-substituents X.[87,88] The latter stabilise benzenethiyl radicals in the following sequence:[88]

$$Cl < H < CH_3 < CH_3O.$$

The stability series of thiyl radicals has also been established by their combined elimination in reactions of ketodithials with tributylstannane:[89]



Thiyl radicals substitute fairly readily different groups linked to polyvalent heteroatoms in organoelement compounds.[90]

III. High-temperature reactions of thiyl radicals

During the last one and a half decades, extensive studies have been carried out on the high-temperature reactions of thiyl radicals with organic compounds.[91–94] They have shown, in particular, that hydrogen sulphide is the most readily available and promising source of thiyl radicals, which subsequently initiate a wide variety of thermal and organic reactions.

1. Thermolysis of hydrogen sulphide

As early as 1852, Cluzel[95] established that hydrogen sulphide decomposes on heating into its constituent elements—hydrogen and sulphur. This process begins at 350–400 °C [96] and becomes appreciable at 1300–1600 °C.[97] The degree of decomposition of hydrogen sulphide is 0.003% at 700 °C,[98] 15–20% at 930 °C,[99] and 83% at 1700 °C.[98] Equilibrium is established after 10 s at 430 °C and after 0.4 s at 930 °C.[99] The thermolysis of hydrogen sulphide is characterised by a small exothermic effect:[100]

$$H_2S \rightarrow H_2 + 0.25S_4, \quad \Delta H^0_{298} = 13 \text{ kcal mol}^{-1}.$$

The energy of the dissociation of hydrogen sulphide into atoms is 173 kcal mol^{-1}.[101] The study of the thermal degradation of hydrogen sulphide in shock waves when it is present at low concentrations in argon revealed the most energy consuming stage:

the dissociation into free radicals with participation of argon molecules:[102,103]

$$H_2S + Ar \xrightarrow{2400-3500\,^{\circ}C} HS^{\cdot} + H^{\cdot} + Ar. \quad (12)$$

The activation energy for reaction (12) is 92 kcal mol^{-1} according to Nagashima[98] or 74 kcal mol^{-1} according to Bowman and Dodge[103] and is close to the dissociation energy of the S–H bond in the hydrogen sulphide molecule: 98.3,[104] 95.0,[105] 81.2,[106] and 92.0 kcal mol^{-1}.[9] The inhibition of the thermolysis of hydrogen sulphide by nitrogen oxide[102] and the initiation of this process by atomic hydrogen[102–107] indicate its radical mechanism. The exothermic reaction of hydrogen sulphide with atomic hydrogen, occurring at a high rate, plays a significant role in the homolytic decomposition of hydrogen sulphide. It also initiates the decomposition of hydrogen sulphide into the elements via the stage involving the generation of sulphydryl radicals:[107]

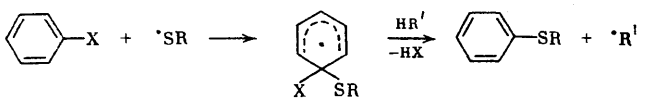
$$H_2S + H^{\cdot} \rightarrow HS^{\cdot} + H_2;$$

$$2HS^{\cdot} \rightarrow H_2S + S; \quad HS^{\cdot} + S \rightarrow H^{\cdot} + S_2. \quad (13)$$

Reaction (13) ensures a low activation energy (37 kcal mol^{-1}) for the thermolysis of undiluted hydrogen sulphide[108] at 400–1000 °C. Under these conditions, hydrogen sulphide does not decompose into the elements via a molecular mechanism in view of the reversibility of the synthesis of H_2S from sulphur and hydrogen.[109]

2. Gas-phase reactions of hydrogen sulphide with aromatic halogeno-compounds and hetero-compounds

The thermal reactions of hydrogen sulphide with aromatic and unsaturated chloro- and bromo-substituted hydrocarbons and their derivatives have been studied in greatest detail. These readily available organic compounds have a high thermal stability[110] and a low reactivity in nucleophilic thiylation.[111] On the other hand, the thermal reactions involving the *ipso*-substitution of a halogen atom in the aromatic ring by sulphydryl and arene- or ethylene-thiyl radicals are promoted by the electrophilic nature of thiyl radicals, the enhanced electron density in the C_{sp^2}–X (X = Cl, Br) bond, the possibility of the formation of an intermediate radical-adduct stabilised with participation of the π-system of the aromatic ring, and also the removal of the halogen atom in the form of a thermally stable hydrogen halide.[112]



X = Cl, Br; R = H, CH_2=CH, Ar

Such reactions were carried out in standard flow systems (empty quartz tube), which model, in terms of their size, the conditions in an ideal displacement reactor.

The gas-phase reaction of hydrogen sulphide with chlorobenzene begins at 550 °C, takes place effectively at 600–700 °C (the degree of conversion of chlorobenzene is 40–90%) with formation of thiophenol, diphenyl sulphide, and benzene. Their ratios are to a large extent determined by the reaction temperature. The yield of thiophenol and diphenyl sulphide reaches a maximum in the narrow temperature range 600–620 °C, above which the formation of benzene increases significantly. In the same temperature range, diphenyl sulphide cyclises partially to dibenzothiophen.[113,114] The excess hydrogen sulphide promotes an increase in the yields of thiophenol, while the excess chlorobenzene increases the yield of diphenyl sulphide.[115–117] The kinetic curves characterise the reaction of chlorobenzene with hydrogen sulphide as a complex process consisting of consecutive-parallel irreversible reactions. Chlorobenzene is converted in succession, via the intermediate formation of thiophenol, into diphenyl sulphide and is at the same time reduced to benzene:[116]

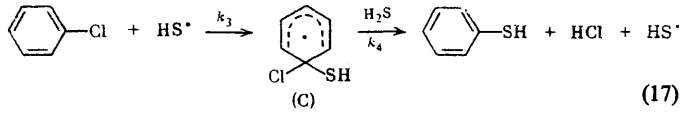
$$C_6H_5Cl + H_2S \xrightarrow{k_1} C_6H_5SH + HCl, \quad (14)$$

$$C_6H_5Cl + C_6H_5SH \xrightarrow{k_2} C_6H_5SC_6H_5 + HCl, \quad (15)$$

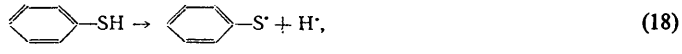
$$C_6H_5Cl + H_2S \rightarrow C_6H_6 + HCl + S. \quad (16)$$

The reaction conditions leading to the maximum yield of thiophenol have been optimised by mathematical experimental design.[115] The yield of C_6H_5SH reaches 30% relative to the initial chlorobenzene and 90% relative to the reacted chlorobenzene at 600–620 °C for the molar ratio H_2S:C_6H_5Cl = 3:1 and a contact time of 38–48 s.

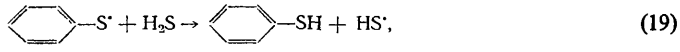
Since the thermolysis of chlorobenzene with dissociation of the C–Cl bond does not yet begin at 600 °C while the dissociation of hydrogen sulphide with formation of thiyl radicals does already occur, on the basis of the kinetic data the mechanism of the formation of thiophenol and diphenyl sulphide can be represented by the following scheme:[118]



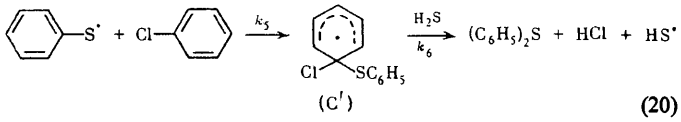
(C) (17)



(18)



(19)



(C′) (20)

According to this scheme, the *ipso*-substitution of the chlorine atom in the aromatic ring by thiyl radicals takes place via a bimolecular chain mechanism. Thiyl radicals are generated preferentially in the chain transfer stages. Radical-adduct formation stages (17) and (20) are slowest. Stage (20) is evidently rate-limiting, since the concentration of benzenethiyl radicals is always lower than that of sulphydryl radicals. This scheme is confirmed by the fact that alkyl chlorides are not thiylated by hydrogen sulphide in the gas phase and are merely reduced. Benzene also does not react with hydrogen sulphide under the conditions investigated.

The Arrhenius expressions for the rate constants for the formation of thiophenol (k_1) and diphenyl sulphide (k_2) via reactions (14) and (15) and as a result of the direct reaction of thiophenol with chlorobenzene (k_2') assume the following form:[118]

$$k_1 = 10^{5.15\pm0.9}\exp[(-27.7\pm0.37)/RT],\ s^{-1},$$

$$k_2 = 10^{8.30\pm0.14}\exp[(-29.0\pm0.6)/RT),\ \text{litre mol}^{-1}\ s^{-1},$$

$$k_2' = 10^{10.17\pm0.63}\exp[(-33.6\pm3.0)/RT],\ \text{litre mol}^{-1}\ s^{-1}.$$

The activation energies for reactions (14) and (15) are similar, which shows that the change in the hybridisation of the carbon atom of the C–Cl bond in chlorobenzene on formation by the latter of the

activated complex (C) or (C′) with a thiyl radical makes the decisive contribution to the activation energy in all cases. The low entropies of activation indicate bimolecular mechanisms of the formation of thiophenol and diphenyl sulphide. The rate constant for the formation of diphenyl sulphide in the chlorobenzene–thiophenol system (k_2') is approximately five times greater than the analogous constant obtained in the chlorobenzene–hydrogen sulphide system.

Eqn. (21) for the constant k_2, obtained by comparing the functional identities of the differential equations describing the real chlorobenzene thiylation process [reactions (14) and (15)] and its mechanism [reactions (17)–(20)], shows that this constant includes also the rate constant for the rate-limiting stage [the formation of the activated complex (C′)] and depends on the ratio of the concentrations of the benzenethiyl radical and thiophenol:

$$k_2 = k_5[C_6H_5S^{\cdot}]/[C_6H_5SH]. \quad (21)$$

The constant k_2 increases on direct interaction of chlorobenzene with thiophenol in the absence of hydrogen sulphide. The excess of the latter promotes the occurrence of reaction (19), as a result of which there is an increase in the concentration of thiophenol [the denominator in Eqn. (21)] and the rate constant for the formation of diphenyl sulphide (k_2) diminishes. This entails an increase in the selectivity of the synthesis of thiophenol by reaction (14).

The initiators and inhibitors of free-radical reactions respectively influence the rate and direction of the reaction of hydrogen sulphide with chlorobenzene. Phenol and cyclohexene retard this reaction, lowering the degree of conversion of chlorobenzene by a factor of 2.[116] Chloromethanes, generating on thermolysis free radicals and carbenes,[119] accelerate the thiophenol formation stage apparently as a result of the additional initiation of the chain decomposition of hydrogen sulphide.[120] An increase in the surface area of the reaction zone lowers the degree of conversion of chlorobenzene without altering the kinetics of its reaction with hydrogen sulphide, which shows that the latter occurs in the bulk phase.

The walls of the reactor promote the generation and destruction of thiyl radicals[116] and the material of the reactor therefore influences significantly the rates of reactions (14) and (15). For the same contact time, the degree of conversion of chlorobenzene in a steel reactor is approximately 30% greater than in a quartz reactor. In this case, the ratio of the reaction products changes in favour of thiophenol and benzene.[121] Evidently the walls of the steel reactor participate in the formation of the radicals $HS^{\cdot}$ and $C_6H_5^{\cdot}$ as a result of the catalysis of the thermolysis of hydrogen sulphide and chlorobenzene by nickel and chromium sulphides and polysulphides,[122] formed on passivation of the reaction surface by hydrogen sulphide. In a copper reactor, hydrogen sulphide does not react with chlorobenzene. The *para*-substituted derivatives of chlorobenzene 4-XC_6H_4Cl react with hydrogen sulphide in the gas phase similarly to chlorobenzene itself. The formation under these conditions of the corresponding thiol 4-XC_6H_4SH and the sulphide $(4\text{-}XC_6H_4)_2S$ indicates the *ipso*-substitution of the chlorine atom by thiyl radicals and confirms the mechanism described by reactions (17)–(20).[123] The following reactions then take place:

$$4\text{-}XC_6H_4Cl + H_2S \rightarrow 4\text{-}XC_6H_4SH + HCl, \quad (22)$$

$$4\text{-}XC_6H_4Cl + 4\text{-}XC_6H_4SH \rightarrow (4\text{-}XC_6H_4)_2S + HCl, \quad (23)$$

$$4\text{-}XC_6H_4Cl + H_2S \rightarrow 4\text{-}XC_6H_5 + HCl + S,$$

$$X = H,\ Cl,\ OH,\ CH_3,\ CF_3. \quad (24)$$

Chloropentafluorobenzene reacts similarly with hydrogen sulphide, affording C_6F_5SH and $(C_6F_5)_2S$. The optimum temperature for the formation of the thiol and the sulphide is determined by the nature of the substituent X (in the case of chlorobenzene) and also by the nature of the benzene ring (in the case of C_6F_5Cl). It decreases with increase in the capacity of the C–Cl bond for homolytic dissociation.

The sequence in which the degree of conversion of the chloro-derivatives increases is identical with the sequence based on the increase in electron density at the chlorine atom. Accordingly, the degree of conversion of 4-XC_6H_4Cl in the reaction with H_2S and also the physicochemical parameters of the C–Cl bond vary in the following sequence of substituents X:

	OH	< Cl	< CF_3	< H	< CH_3
Charge Q (Cl), eV	−0.16	—	0.15	−0.17	−0.17
$\nu(^{35}Cl$ NQR), cm^{-1}	34.9	34.8	34.7	34.65	34.5
$\delta[^{13}C(C^1)]$ relative to X = H, p.p.m.	−8.74	−1.71	3.88	0.00	−3.21
Charge on C^1 (π) atom, eV	−0.04	—	3.03	0.00	−0.02

The ratio of the thiylation products (thiol/sulphide) depends significantly on the reactivity of the intermediate thiol. It is correlated with parameters of the electronic structure of the compounds 4-XC_6H_4SH and their reactivity, increasing in the following sequence of substituents X:

$$Cl < CH_3 < H < CF_3 < OH.$$

$C_5F_5Cl[\nu(^{35}Cl$ NQR) = 39.4 $cm^{-1}]$ reacts most slowly with hydrogen sulphide among all the *para*-substituted chlorobenzenes. The thiol/sulphide ratio in the thiylation products is highest in this instance.

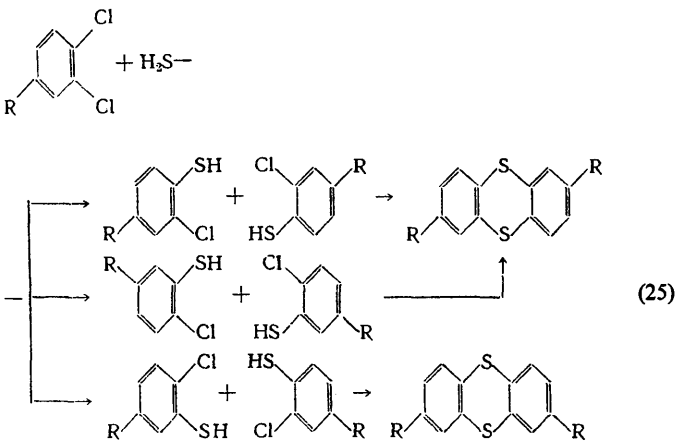
The reactivity of these thiols is largely determined by the degree of localisation of the HOMO on the sulphur atom, since the other parameters of the electronic structure (the ionisation potential and the charge on the sulphur atom) depend little on the nature of the substituent X or the benzene ring.

The degree of localisation of the HOMO on the sulphur atom is correlated only with the resonance component of the substituent X, increasing with decrease in its electron-donating capacity. The thiol/sulphide ratio is correlated directly with the degree of localisation of the HOMO on the sulphur atom of the thiol, diminishing with enhancement of the π-electron-donating properties of the substituent X. Thus the π-electron-accepting substituents X in the thiol 4-XC_6H_4SH decrease the reactivity of the thiol in its interaction with the initial chloro-derivative [scheme (23)], while π-electron-donating substituents increase it. From the standpoint of the free-radical mechanism of reactions (22) and (23), the formation of the arenethiyl radical, which then participates in the second stage of scheme (20) under the conditions of the competing interaction with H_2S [see scheme (19)], determines the capacity of this radical for stabilisation.

It has been suggested that the distribution of the unpaired electron in 4-$XC_6H_4S^{\cdot}$ is analogous to the distribution of the HOMO in 4-XC_6H_4SH, so that π-electron-donating substituents X stabilise the arenethiyl radicals, whilst π-electron-accepting substituents destabilise them, as a result of which in the latter case the radicals are formed at a lower rate and subsequently react preferentially with hydrogen sulphide in accordance with scheme (19) and not with the initial chloro-derivatives in accordance with scheme (20). 4-Hydroxythiophenol is an exception, which is evidently associated with the autoinhibition of the free-radical process in this case. By increasing the dehydrating activity of the 4-$XC_6H_4S^{\cdot}$

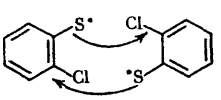
radical, π-electron-accepting substituents X promote the formation of the thiol 4-XC_6H_4SH via scheme (22) with a high selectivity (for a low degree of conversion of the initial chloride). C_6F_5SH is formed with the highest selectivity. *ortho*-Substituted chlorobenzenes react with hydrogen sulphide in the gas phase via pathways different from those for the *para*-substituted derivatives. The main product of the thiylation of 2-chlorotoluene or chloromesitylene is the corresponding thiol [scheme (14)], since the steric effect of the *ortho*-ethyl group hinders the interaction of the 2-methylbenzenethiyl or mesitylenethiyl radical in the sulphide formation stage via scheme (20).[124]

The interaction of 1,2-dichloro- or 1,2,4-trichloro-benzenes with hydrogen sulphide results in the formation of a thianthrene or dichlorothianthrenes respectively according to scheme (25):[125]



(25)

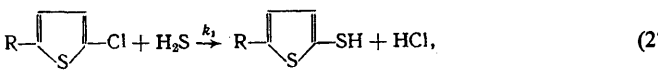
Their formation is apparently determined by the intermolecular cyclisation of *ortho*-chloro-substituted benzenethiyl radicals proceeding via scheme (26) at a high rate:



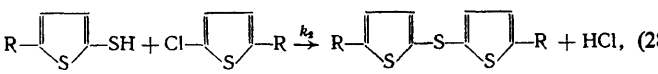
(26)

In contrast to *p*-chlorophenol, *o*-chlorophenol reacts with hydrogen sulphide more effectively and with a more selective formation of 2-hydroxythiophenol in accordance with scheme (22).[126]

The reaction of hydrogen sulphide with 2-chlorothiophen, leading to thiophen-2-thiol and di(2-thienyl)sulphide takes place at lower temperatures (500–540 °C) than in the case of chlorobenzene:[127]



(27)



(28)

R=H, Cl, C_2H_5.

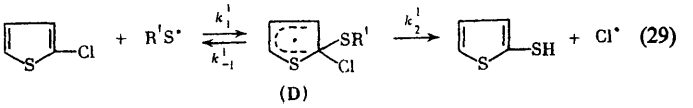
Reaction (28), leading to the sulphides, then proceeds at a higher rate than in the case of chlorobenzene [scheme (14)].

Arrhenius expressions have been obtained for the rate constants k_1 and k_2 for the formation of thiophen-2-thiol and di(2-thienyl)-sulphide [schemes (27)–(28)]:

$$k_1 = 10^{14.2\pm0.4}\exp[(-52.0\pm3.4)\times10^3/RT],\ s^{-1},$$

$$k_2 = 10^{13.8\pm0.2}\exp[(-55.7\pm2.9)\times10^3/RT],\ mol^{-1}\ s^{-1}.$$

The high activation energies for both reaction stages and the high pre-exponential factors indicate a unimolecular mechanism of the reaction. This can be due to the faster attack by the thiyl radicals HS˙ and RS˙ on the polarised double bonds of the thiophen ring and the greater stability of the activated complex (D), which decomposes slowly in the rate-limiting stage in accordance with scheme (29):[128]



(29)

(D)

R^1 = H, R.

5-Ethylthiophen-2-thiol is formed from 2-chloro-5-ethylthiophen via schemes (27) and (28) in a higher yield and 5-chlorothiophen-2-thiol is formed from 2,5-dichlorothiophen in a lower yield than that of thiophen-2-thiol formed from 2-chlorothiophen. In the absence of hydrogen sulphide, 2,5-dichlorothiophen dehydrodimerises at 560–570 °C to tetrachloro-3,3′-bithienyl.[129]

The reaction of hydrogen sulphide with bromobenzene begins at 500 °C, i.e. at a temperature lower by 50 K than the reaction of H_2S with chlorobenzene. At all the temperatures investigated, the degree of conversion of bromobenzene is higher than that of chlorobenzene, while the products of the reaction with hydrogen sulphide are similar. However, their ratios and yields differ.[130] The reactions of hydrogen sulphide with bromobenzene and its substituted derivatives lead mainly to the corresponding sulphides [via schemes analogous to schemes (22) and (23)].

The bromo-derivatives of condensed aromatic hydrocarbons (naphthalene, anthracene, phenanthrene) react with hydrogen sulphide even in the liquid phase at 150–250 °C,[131] forming only the corresponding sulphides.

Iodobenzene reacts with hydrogen sulphide already at 480 to 500 °C, being converted preferentially into diphenyl sulphide and benzene. Thiophenol and diphenyl disulphide are formed in small amounts in addition to the above compounds. In the interaction of halogenobenzenes with hydrogen sulphide, the optimum temperature for the formation of thiophenol and diphenyl sulphide decreases with increase in the atomic number of the halogen:

Cl (600—620° C) > Br (550—580° C) > I (480—500° C).

The degree of conversion of the halogeno-derivative increases and the thiol/sulphide ratio decreases in the same sequence. The sequence in the variation of the mobility of the halogen corresponds to the variation of the C–X bond strength in halogenobenzenes (Table 1) and is characteristic of radical reactions.[132] Fluorobenzene does not react with hydrogen sulphide even at 700 °C. Above this temperature, it is partly converted into a mixture of isomeric mono- and di-fluorobiphenyls.

3. Gas-phase reactions of thiophenol with aromatic and heteroaromatic halogeno compounds

Thiophenol interacts with aromatic halogeno-derivatives at 400–600 °C primarily with formation of asymmetric aromatic sulphides in accordance with the general mechanism[133]

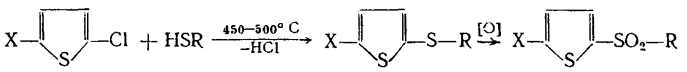
$$C_6H_5SH + RX \rightarrow C_6H_5SR + HX, \quad (30)$$

R = aryl, thienyl, naphthyl; X = Cl, Br.

Reaction (30) is favoured by an excess of the halogeno-derivatives and the lowest possible temperature. With increase in temperature and in the concentration of thiophenol, processes involving the reduction of the halogeno-derivative, exchange reactions, and

cyclisation reactions of diaryl sulphides and thiyl radicals are accelerated. The reactions of thiophenol with *ortho*-substituted halogenobenzenes are accompanied by the formation of sulphur-containing heterocyclic compounds: thus the interaction of thiophenol with 2-chlorotoluene led to the isolation of thioxanthrene,[134] the interaction with *o*-dihalogenobenzene afforded thianthrene,[125] and the interaction with *o*-chlorobenzene gave rise to 4-hydroxydibenzothiophen.[135]

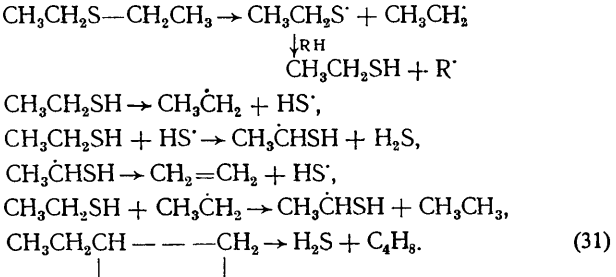
Many asymmetric aryl thienyl sulphides were obtained for the first time by the reaction of aromatic thiols with 2-chlorothiophen and its 5-substituted derivatives[136] (yield 44–76%):



$X = H,\ C_2H_5,\ Cl;$
$R = C_6H_5,\ 4\text{-}H_3CC_6H_4,\ 1\text{-}C_{10}H_7.$

4. Gas-phase reactions of alkanethiols, dialkyl sulphides, and dialkyl polysulphides with aromatic halogeno-compounds

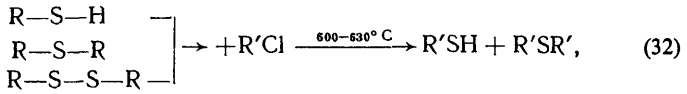
The readily available alkanethiols, dialkyl sulphides and polysulphides, or their mixtures can be used as sources of thiyl radicals for the interaction of the latter with aromatic halogeno-compounds. The thiols and sulphides decompose in the gas phase with formation of hydrogen sulphide and alkenes via a free-radical mechanism with the immediate generation of thiyl radicals,[137] for example:



(31)

$D_{C_2H_5SH}(C-S) = 63.5$ kcal mol^{-1};
$D_{H_2S}(S-H) = \sim 90$ kcal mol^{-1}.

The high-temperature reactions of alkanethiols, dialkyl sulphides, and dialkyl disulphides with chloro-derivatives of benzene, thiophen, and naphthalene lead to the same thiylation products as in the case where hydrogen sulphide is used.[138–140] This indicates a unique mechanism of reactions involving the participation of thiyl radicals according to schemes (17)–(20):



(32)

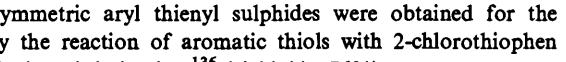
$R = Alk;\ R' = C_6H_5,\ 4\text{-}CH_3C_6H_4,\ 4\text{-}ClC_6H_4,\ 2\text{-}ClC_6H_4,$
$4\text{-}CF_3C_6H_4,\ C_6F_5,\ 3,4\text{-}Cl_2C_6H_3,\ C_{10}H_7,\ C_4H_3S.$

The reactions of alkanethiols with aryl halides differ by the increased selectivity in the formation of the thiol R'SH [scheme (32)]. The alkenes formed via scheme (31) probably inhibit the rate-limiting stage in the formation of the sulphide R'SR'.

IV. Liquid-phase thermal reactions of thiyl radicals

Thiyl radicals can be generated in the liquid phase from diaryl disulphides, arenethiols, and the sulphur–hydrogen sulphide system even at moderately high temperatures (100–250 °C).

Heating of diphenyl disulphide with bromoarenes at 125–230 °C in hydrogen sulphide at atmospheric pressure leads to the corresponding aryl phenyl sulphides:[141]



$Ar = C_6H_5,\ 2\text{-}HOC_6H_4,\ 4\text{-}HOC_6H_4,\ 4\text{-}C_2H_5OC_6H_4,$
$C_{10}H_7,\ 2\text{-}HOC_{10}H_6.$

Aromatic chloro-compounds and 2-chlorothiophen hardly enter into reaction (33), which is apparently due to the high strength of the C–Cl bond, the boiling points of the initial reactants being inadequate for the homolysis of the latter. The temperature of the thiylation of bromoarenes in accordance with scheme (33) diminishes after the introduction of a π-electron-donating substituent into the benzene ring. Above this temperature, the reactions leading to the reduction of the halogeno-derivative to the corresponding aromatic hydrocarbon are accelerated. Thiophenol and diphenyl sulphides are formed simultaneously in a low yield from diphenyl disulphide as a result of thermolysis and hydrothiolysis.

Reaction (33) is initiated by the free radicals formed in the thermolysis of the initial compounds:

(33)

(34)

(35)

(36)

(37)

(38)

Reactions (34)–(36) of free radicals with H_2S lead to the formation of thiophenol and the products of the reduction of Br$^{\cdot}$ and Ar$^{\cdot}$. In the reactions of the latter with thiophenol, which is a stronger H-donor than hydrogen sulphide, benzenethiyl radicals are generated. They are responsible for the chain thiylation of ArBr via scheme (20).

The radicals $C_6H_5S^{\cdot}$ play the role of agents transferring hydrogen atoms from hydrogen sulphide to the radicals Br$^{\cdot}$ and Ar$^{\cdot}$ in reaction (33).

When thiophenol is heated with aryl bromides, the corresponding aryl phenol sulphides are also formed [see schemes (37), (38), and (20)].[142] However, a more limited amount of bromide enters into the reaction with thiophenol, which is due to the inadequately high boiling point of the reaction mixture (the boiling point of thiophenol is 180 °C).

Fairly simple methods of synthesis of aryl phenyl sulphides have been developed on the basis of the reactions of Ph_2S (in H_2S or thiophenol) and ArBr.

Thiophen-2-thiol and 1-thionaphthol do not react with aryl bromides in the liquid phase to form the corresponding sulphides. The initial bromides are merely reduced to the corresponding aromatic hydrocarbons, while the thiols are then converted into symmetrical sulphides. This shows that the thiophen-2-thiyl and naphthalene-1-thiyl radicals are weaker hydrogen atom transferring agents than the benzenethiyl radical. Overall, this disturbs the process and leads to the termination of the chain transfer stage.

The sulphydryl radicals HS$^{\cdot}$ can be generated on interaction of elemental sulphur with hydrogen sulphide even at 110–230 °C. Thus 1-chloronaphthalene, 1-bromo-4-chlorobenzene, and 4-bromotoluene react in accordance with scheme (39) with the sulphur–hydrogen sulphide system at 180–230 °C, forming the corresponding diaryl sulphide in 8–88% yield:[43]

$$ArX \xrightarrow[180-230^{\circ}C]{H_2S+S} Ar_2S + HX. \quad (39)$$

The reaction of 4-bromophenol with the S + H_2S system takes place already at 110–125 °C, being completed after 2 h by the formation of di(hydroxyphenyl) sulphides and phenol.

At 200 °C, 4-chlorophenol reacts with hydrogen sulphide and sulphur via the same pathway, but the reaction is completed after 45 h. 2-Bromophenol reacts with the S + H_2S system more slowly than does 4-bromophenol and at a higher temperature (200 °C):[144]

$$H_2S + S \rightleftarrows 2HS^{\cdot},$$

$$4\text{-}BrC_6H_4OH + HS^{\cdot} \xrightarrow[110-125^{\circ}C]{H_2S} 4\text{-}HOC_6H_4SH + HBr + HS^{\cdot}, \quad (40)$$

$$4\text{-}BrC_6H_4OH + 4\text{-}HOC_6H_4SH \rightarrow (4\text{-}HOC_6H_4)_2S + HBr + HS^{\cdot},$$

$$4\text{-}HOC_6H_4Br \rightarrow 4\text{-}HOC_6H_4^{\cdot} + Br^{\cdot},$$

$$4\text{-}HOC_6H_4^{\cdot} + H_2S \rightarrow C_6H_5OH + HS^{\cdot}. \quad (41)$$

The nature of the halogen atom in the molecules of aryl halide influences the rate and direction of the liquid-phase reaction of aryl halides with the S–H_2S system in the same way as it affects the rate of their reaction with gaseous hydrogen sulphide. This confirms that HS$^{\cdot}$ radicals are generated from hydrogen sulphide in the presence of sulphur and react with halogenoarenes via schemes (40) and (41) under mild conditions.

V. Reactions of hydrogen sulphide, thiols, and dialkyl sulphides and polysulphides with halogenoalkenes

At 400–550 °C, hydrogen sulphide condenses with halogenoalkenes. The simplest of these (vinyl chloride) reacts with hydrogen sulphide at 530–560 °C to form ethylenethiol and thiophen. In the presence of an excess of hydrogen sulphide ethylenethiol is the main reaction product (yield 60%), while in the presence of an excess of vinyl chloride mainly thiophen is formed (yield 60–80%):[145]

$$CH_2{=}CHCl + H_2S \rightarrow CH_2{=}CHSH + HCl, \quad (42)$$

$$CH_2{=}CHCl + HSCH{=}CH_2 \xrightarrow{-HCl} \xrightarrow{-H_2} . \quad (43)$$

At the outlet for the gas phase, ethylenethiol is stabilised by being cooled to −70 °C after which it is warmed rapidly and analysed.[146] It trimerises rapidly at room temperature.

Reactions (42) and (43) proceed with participation of thiyl radicals which add to the carbon atom of the double bond of the halogenoalkene linked to the halogen atom. This leads to the *ipso*-substitution of the latter via the following scheme:

$$CH_2{=}CHCl + HS^{\cdot} \rightarrow {}^{\cdot}CH_2{-}CH(Cl)SH \xrightarrow{H_2S} CH_2{=}CHSH + HCl + HS^{\cdot}$$

$$\xrightarrow[-HCl]{} CH_2{=}CHS^{\cdot} \xrightarrow{CH_2=CHCl} \rightarrow \left[\text{Cl-thiophenyl}\right] \xrightarrow[-HCl,\ -H^{\cdot}]{H_2S} \text{thiophen} \quad (44)$$

(A)

(A) $\xrightarrow[-HCl,\ -HS^{\cdot}]{H_2S}$ thiophen $\xrightarrow{-H_2}$ thiophen

The ethylenethiyl radical is generated thermally from the primary product of reaction (44)—ethylenethiol. The radical then initiates the chain thiylation of vinyl chloride. Thiophen can be the product of the cyclisation of the radical-adduct (A) or of divinyl sulphide. Scheme (44) is confirmed by the fact that neither ethylene nor acetylene react with hydrogen sulphide under analogous conditions. This is also confirmed by the pathway followed in the reactions of dichloroethylenes with hydrogen sulphide and its organic derivatives (see below).

In contrast to vinyl chloride, vinyl bromide reacts with hydrogen sulphide at 450–500 °C to form only ethylenethiol (regardless of the reaction conditions[147]) in accordance with scheme (42). This may be due to the inhibiting effect of the hydrogen bromide evolved during the reaction. Being a stronger hydrogen donor than hydrogen sulphide, it reacts rapidly with the ethylenethiyl radical, as a result of which the latter does not participate in the stages of reaction (44) leading to thiophen.

The reactions of dichloroethylene with hydrogen sulphide take place mainly in accordance with schemes (42)–(44). However, under these conditions a mixture of organosulphur compounds is formed, which is due to the secondary reactions of labile intermediates. The interaction of 1,2-dichloroethylene with hydrogen sulphide is illustrated by scheme (45), which explains the formation of all the reaction products detected:[148]

$$ClCH{=}CHCl + H_2S \rightarrow ClCH{=}CHSH + HCl,$$

$$ClCH{=}CHSH + ClCH{=}CHCl \rightarrow ClCH{=}CHSCH{=}CHCl + HCl,$$

$$2ClCH{=}CHSCH{=}CHCl \rightarrow \text{Cl-thiophenyl} + \text{Cl-thiophenyl} + 2HCl,$$

Cl-thiophenyl + H_2S → SH-thiophenyl + HCl,

SH-thiophenyl + ClCH=CHCl → SCH=CHCl-thiophenyl $\xrightarrow{-HCl}$

→ thiophen + thiophen (45)

An excess of 1,2-dichloroethylene promotes the preferential formation of 2- and 3-chlorothiophens, whose yield reaches 30–35%.

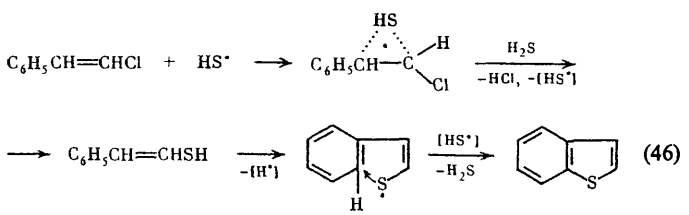
A mixture of 2- and 3-chlorothiophens, thiophen, thiophen-2-thiol, thiophen-3-thiol, thienothiophens, and vinyl sulphides is formed from 1,1-dichloroethylene and hydrogen sulphide at 470–550 °C via schemes analogous to scheme (45).[149] However, the sulphides obtained under these conditions contain a chlorine atom not in the β-position but in the α-position relative to the sulphur atom. This shows that the primary product of the reaction of 1,1-dichloroethylene with hydrogen sulphide is α-chloroethylenethiol, from which the α-chloroethylenethiyl radical, responsible for the formation of all the subsequent reaction products, is generated:

$$CH_2{=}CCl_2 + HS^{\cdot} \rightarrow {}^{\cdot}CH_2CCl(SH)_2 \xrightarrow[-HCl,\ -[HS^{\cdot}]]{H_2S} \xrightarrow{-HCl} CH_2{=}CClSH \rightarrow CH_2{=}CClS^{\cdot}$$

The regiospecificity of the thermal addition of thiyl radicals to halogenoalkenes, namely to the carbon atom linked to the halogen atom, is unambiguously demonstrated in this case.

The reaction of trichloroethylene with hydrogen sulphide in the gas phase does not lead to sulphur-containing compounds.[150] The reaction of tetrachloroethylene with hydrogen sulphide at 450 °C leads to tetrachlorothiophen (yield 75%) but it is slower than in the case of other chloroalkenes having polarised double bonds.[151]

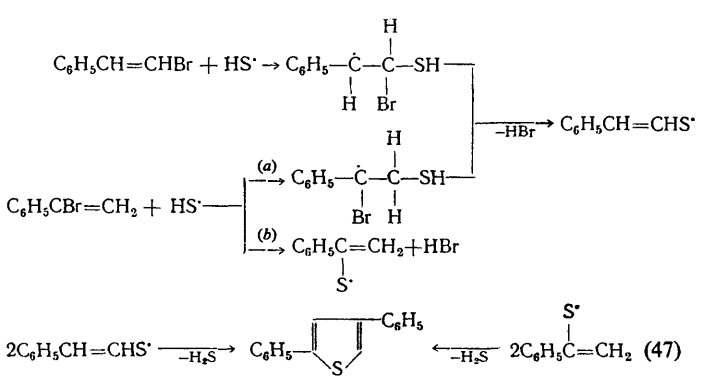
Virtually the only product of the reaction of β-chlorostyrene with hydrogen sulphide at 600 °C is benzo[*b*]thiophen (yield 85%). The 2-phenylethylenethiol formed initially readily generates the 2-phenylethylenethiyl radical (stabilised as a result of the π,π-conjugation of the ring and the double bond), which undergoes intramolecular condensation to benzothiophen at a high rate:[152,153]



(46)

Instead of β-chlorostyrene, its gas-phase precursor (αβ-dichloroethylbenzene) can be introduced into reaction (46), and instead of hydrogen sulphide lower alkanethiols can be introduced.

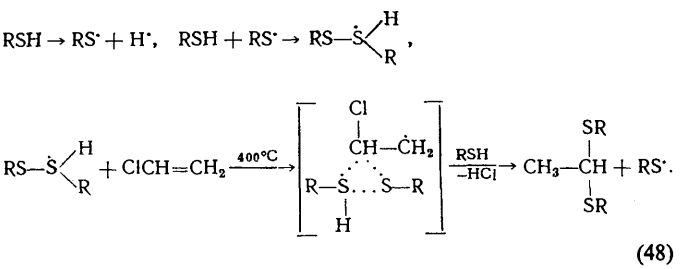
In the liquid phase, boiling β-chlorostyrene does not react with hydrogen sulphide, whereas α- and β-bromostyrenes interact with hydrogen sulphide in the liquid phase even at 150–170 °C, affording mainly 2,4-diphenylthiophen (yield 37%). Apparently in the liquid phase phenylethylenethiyl radicals undergo merely intermolecular condensation, leading to the same product of reaction (47)—2,4-diphenylthiophen[154] (the cage effect and the fairly high concentration of radicals at the instant of formation exert an influence):



(47)

Benzothiophen is formed in the gas phase in 76% yield from β-bromostyrene and hydrogen sulphide and in 9% yield from α-bromostyrene and hydrogen sulphide. In the latter case, the β-phenylethylenethiyl radicals are formed to some extent, but this direction of attack by the thiyl radical HS˙ on the halogenoalkene molecule takes place to an insignificant degree [scheme (47), pathway (*b*) is preferred to pathway (*a*)] even when a radical-adduct of the benzyl type is formed.

Organic derivatives of hydrogen sulphide (thiols, dialkyl sulphides, and dialkyl disulphides) react with halogenoalkenes both in the gas phase and in the liquid phase. The products of their reactions with vinyl chloride at 400 °C are 1,1-di(alkylthio)ethanes (yield 10–33%), formed as a result of the preliminary thermal condensation of alkanethiyl radicals with the initial sulphide reagent via scheme (48):[155]



(48)

Alkyl vinyl sulphides are not intermediates in the formation of dithioacetals under these conditions, since the thermal addition of alkanethiols to them under analogous conditions leads to the usual anti-Markovnikov adducts. On the other hand, the conversion of 1,2-di(alkylthio)ethanes to the isomeric dithioacetals is also not observed under these conditions:

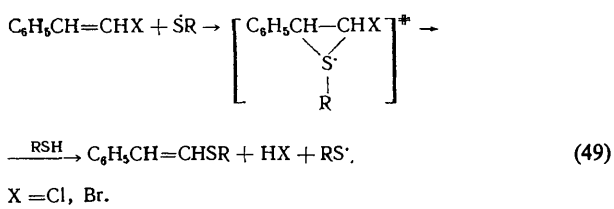
$$RSH + CH_2{=}CHSR \rightarrow RSCH_2{-}CH_2SR.$$

The gas-phase reactions of vinyl chloride with aromatic thiols and thiophen-2-thiol lead to the corresponding aryl vinyl sulphides or 2-thienyl vinyl sulphide respectively. The selective occurrence of this reaction is promoted by a large excess of the chloro-derivative:[156]

$$RSH + ClCH{=}CH_2 \xrightarrow{350\text{–}450\,^\circ C} \underset{60\text{–}90\%}{RS{-}CH{=}CH_2} + HCl,$$

$R = C_6H_5$, 4-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 1-$C_{10}H_7$, 2-C_4H_3S.

Aromatic thiols and thiophen-2-thiol react with β-chloro- and β-bromostyrenes in the liquid phase even at 80–160 °C with formation of 1-phenyl-2-arylthio- or 1-phenyl-2-thienylthio-ethylenes respectively (yield 70–95%):[157]

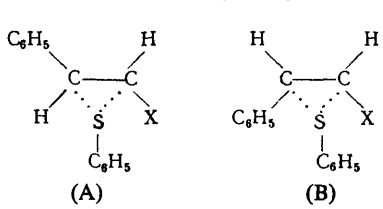


(49)

X = Cl, Br.

Reaction (49) begins already at 80 °C and proceeds efficiently at 140–160 °C.

At 80–100°, only the *trans*-isomer of the β-halogenostyrene enters into reaction (49), whilst at 140–160 °C both isomers react. The process takes place rigorously stereospecifically, which is apparently due to the stabilisation of the radical-adduct with participation of the β-phenylthio-group. The transition state (A), which is sterically less strained than the state (B), is then formed from the *trans*-isomer of the β-halogenostyrene:



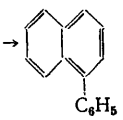
(50)

Thiophenthiol reacts with β-bromostyrene more slowly than with β-chlorostyrene owing to the inhibiting effect of hydrogen bromide, which functions as a trapping agent for thiyl radicals and initiates

the decomposition via scheme (51) of the sulphide formed:

$$C_6H_5S^{\cdot} + HBr \rightleftarrows C_6H_5SH + Br^{\cdot},$$

$$2C_6H_5CH{=}CHSC_6H_5 + 2Br^{\cdot} \rightarrow \left[2C_6H_5\dot{C}H{-}\underset{\displaystyle Br}{\underset{|}{C}}HSC_6H_5\right] \rightarrow$$



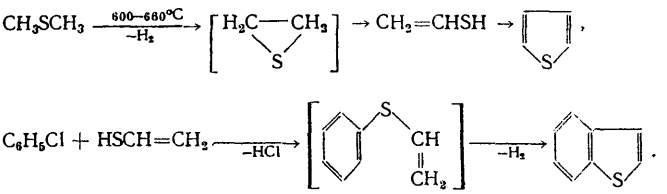
$$+2C_6H_5SH + 2HBr. \qquad (51)$$

In particular, 1-phenyl-2-naphthylthioethylene and 1-phenyl-2-thienylthioethylene have been obtained via scheme (51).

VI. Thermal synthesis of thiophen and its derivatives and analogues

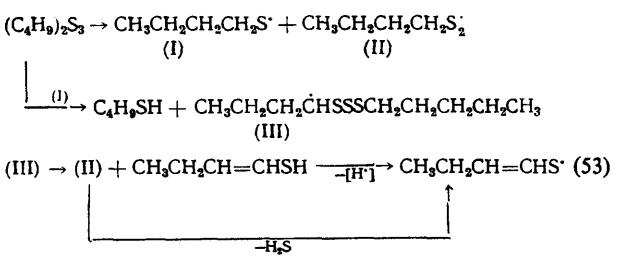
The study of the thermal reactions of thiyl radicals generated from different types of organic sulphur compounds has made it possible to develop a wide variety of methods of synthesis of thiophen, benzothiophen, dibenzothiophen, thianthrene, thioxanthene, and other sulphur-containing heterocycles. They are all based on thermal cyclisations and condensations of different types of αβ-unsaturated thiyl radicals.[158] Some of these methods have already been mentioned (see Section III above).

Thiophens are the products of the thermolysis of dialkyl sulphides, which decompose in accordance with a unique mechanism which includes a stage involving the generation of ethylenethiol. The ethylenethiyl radical formed from the latter undergoes intermolecular condensation to a thiophen, for example, in accordance with the following scheme:[159,160]



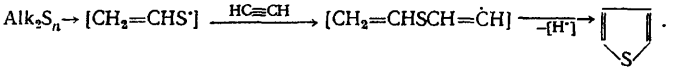
(52)

Thiophen is also formed in the pyrolysis of vinyl sulphides and dialkyl polysulphides.[161,162] The dibutyl polysulphides $(C_5H_9)_2S_n$ are thermolysed to thiophen most selectively under these conditions:[162]

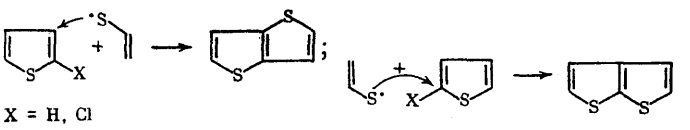


For n = 3, the maximum yield of thiophen reaches 43% at 500–520 °C. According to scheme (53), the trisulphide molecule is in fact the richest source of butenethiyl radicals, which subsequently cyclise to thiophen.[161]

Acetylene is an effective trapping agent for ethylenethiyl radicals. Its cothermolysis with low-molecular-weight dialkyl polysulphides at 470–520 °C leads to thiophen (yield up to 62%):[169]



Two isomeric thienothiophens are then formed together with thiophen, apparently as a result of the interaction of the ethylenethiyl radical with the thiophen ring (in proportions of 1 : 1):

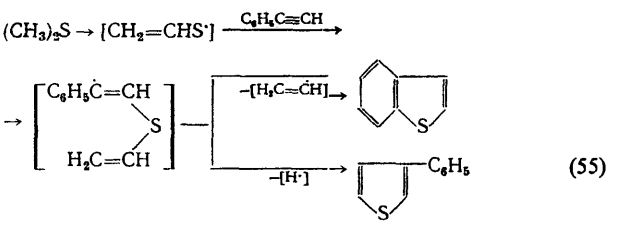


X = H, Cl

(54)

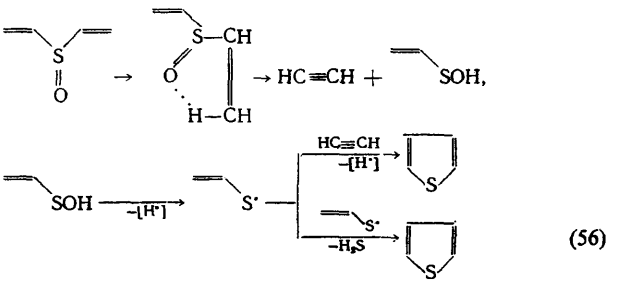
The cothermolysis of 2-chlorothiophen with a mixture of diethyl polysulphides also results in the formation, in accordance with scheme (54), of isomeric thienothiophens, but the [2,3-*b*]-isomer predominates in it.[164] This confirms the preferential attack by the thiyl radical on the sp^2-hybridised carbon atom linked to the halogen atom.

The cothermolysis of phenylacetylene with dimethyl sulphide at 450–500 °C leads to 3-phenylthiophen and benzo[*b*]thiophen in accordance with the following scheme:[165]



(55)

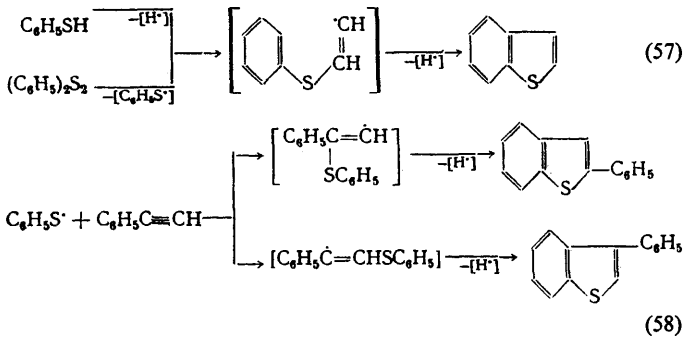
The main product of the gas-phase thermolysis of divinyl sulphoxide is thiophen, whose maximum yield (60%) is attained at 400 °C.[166] The mechanism of reaction (56) includes a stage in which ethylenethiyl radicals are generated:



(56)

Thiophenol reacts with acetylene at 550–590 °C, while diphenyl disulphide reacts at 500 °C with selective formation of benzo[*b*]thiophen. The products of the reaction of phenylacetylene with diphenyl disulphide are 2- and 3-phenylbenzo[*b*]thiophen (in proportions of 1 : 1.5). The mechanisms of reactions (57) and (58) include stages in which benzenethiyl radicals are generated and

add to multiple bonds:[167]



(57)

(58)

VII. Conclusion

The study of the thermal generation and reactivity of thiyl radicals established the following features:

1. The radicals HS$^{\cdot}$, $CH_2{=}CHS^{\cdot}$, and ArS$^{\cdot}$, generated from hydrogen sulphide and its organic derivatives, readily enter into reactions involving the *ipso*-substitution of the halogen atom linked to the sp^2-hybridised carbon atom.

2. Alkanethiyl radicals are incapable of such reactions. However, they undergo thermal condensation with alkanethiols, dialkyl sulphides, and dialkyl disulphides with formation of the corresponding sulphuranyl radicals $R\dot{S}_nR_2$. The latter are trapped in the gas phase by halogenoalkanes with formation dithioacetals.

3. Ethylenethiyl radicals undergo intramolecular or intermolecular cyclisation in the gas phase to heterocyclic compounds of the thiophen and benzothiophen series.

4. Acetylene and phenylacetylene are effective trapping agents for thiyl radicals. The sulphydryl radicals HS$^{\cdot}$ do not react with alkynes, alkenes, and arenes in the gas phase, but readily add to the multiple bonds of halogenoalkenes and halogenoarenes.

The observed features of the thermal reactions of thiyl radicals with organic compounds are important for the elucidation of the mechanism of the formation of sulphur-containing components of petroleums, coal, shale, and natural gas and also the products of their heat treatment.

Numerous methods for the synthesis of a wide variety of organic sulphur compounds have been developed on the basis of the reactions of thiyl radicals investigated. Many of them can be achieved on an industrial scale using readily available intermediates and sulphur-containing waste of the petrochemical, coal-chemical, chemical gas, and cellulose-paper industries.

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Polymer photostabilisers. Photophysical properties and stabilising efficiency

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ABSTRACT. The photophysical characteristics and luminescence-spectroscopic properties of molecules with a high photostabilising efficiency are examined. It is shown theoretically that the short lifetime and (or) low population of the triplet state of the molecule are essential (but not sufficient) conditions for its use as a photostabiliser. Both these conditions or one of them are fulfilled when systems in which non-radiative conversion processes, initiated by adiabatic reversible photochemical processes or systems with heavy atoms, are used. Experimental data confirming these postulates are presented.

The bibliography includes 218 references.

Contents

I. Introduction 792
II. Photophysical processes in polyatomic molecules 793
III. Initiation of non-radiative conversion processes by adiabatic photochemical reactions 794
IV. Photophysical properties of effective photostabilisers 797
V. Principal structural types of photostabiliser molecules 799
VI. Synergistic mixtures of photostabilisers 802

I. Introduction

The problem of increasing the photostability of polymeric materials has not lost its interest over a long period of time despite the advances achieved both in the understanding of the scientific principles of the problem and in the practical application of the results.[1–4] The reason for this is the expansion of the range of polymeric materials and their applications together with increasing requirements for their photostability, including photostability under extreme conditions.

One of the most common and promising ways of solving the problem involves the use of special additives which are introduced into polymers and polymer compositions to increase their photostability. In terms of the mechanism of their protecting action, the additives can be divided (albeit not entirely unambiguously) into two types: compounds whose action has a chemical mechanism and systems whose stabilising effect is manifested already in the initial, physical stage of the polymer phototransformation process.

The role of compounds with a chemical stabilisation mechanism involves chemical reactions of their molecules with the products of the photolysis of polymers (usually radicals) and convert the latter into an inactive state, interrupting the chain of transformations. Such compounds can be used to protect not only against the action of light but also against other factors which induce the appearance of radical polymer degradation processes (oxidation, the action of heat, mechanical stress, ionising radiation, etc.). Compounds of this type include antioxidants and thermostabilisers.

Compounds with the physical photostabilisation mechanism prevent the occurrence of the primary stage of the photolysis of polymer or impurity molecules. These compounds are intrinsic photostabilisers and in employing this term below we shall have only them in mind.

The significant advances achieved during the last decades in the creation of antioxidants and associated to a large extent with the development and introduction of a new class of stabilisers — sterically hindered amines (SHA)[3,4]—have not reduced the interest in the study and practical employment of photostabilisers. This has arisen for a number of reasons.

Photostabilisers include compounds of different classes with a broad range of protecting properties and which absorb the energy of the light radiation in different spectral regions. In contrast to the sterically hindered amines, photostabilisers have more universal applications: they can be used both for carbochain and for different kinds of heterochain polymers which undergo a short chain of photochemical transformations — in filled, dyed, and incombustible polymers. Sterically hindered amines and other compounds with a chemical stabilisation mechanism have a limited period of activity, because they are consumed after a time. The mechanism of the action of photostabilisers in the absence of side processes does not involve their consumption and can ensure a long operating life of the polymer. Photostabilisers are able to manifest a synergistic effect in mixtures with stabilisers whose action has a chemical mechanism, which makes it possible to increase the lifetime of polymeric materials and to reduce the concentration of additives.

It is noteworthy that the requirements imposed on the molecular and electronic structures of effective photostabilisers are the same or are similar to the requirements which must be satisfied by intrinsically photostable polymers (see Section IV). The development of ideas about the mechanism of the action and causes of the high efficiency of photostabilisers has thus promoted the elucidation of ways of creating photostable polymer molecules. The study of the physical stages in the stabilisation process is important also for antioxidant molecules, because on formation of complexes with electronically excited molecules (for example, with the O_2 molecule[5,6]) many of them induce their quenching. All the foregoing discussion demonstrates the current interest of the study of the mechanism of the action of photostabilisers and of the principles of their selection.

Two physical processes underlie the action of photostabilisers: the process involving the absorption of light by the stabiliser which shields the polymer molecule against the action of incident photons and the transfer of energy from the electronically excited polymer molecules to the stabiliser molecules with their subsequent deactivation. Systems in which the former process occurs preferentially are called absorbers (UV absorbers), while systems of the latter type are called quenching agents. The determination of the leading mechanism of the stabilisation process is important for the selection of the stabiliser. UV absorber photostabilisers should evidently absorb the light which photolyses the polymer molecules. The essential condition for the effective action of quenching agent molecules is the overlap of the luminescence spectrum of the polymer and of the absorption spectrum of the stabiliser.[1,2,7–12]

However, by no means all molecules satisfying these requirements can be effective photostabilisers. Furthermore, these conditions can be satisfied also by molecules of photosensitisers of the decomposition of polymers. The molecule of the effective photostabiliser should possess also a definite set of photophysical properties. Theoretical analysis of this problem is the subject of the present review. Clearly, with this formulation of the problem one can elucidate only the necessary but not sufficient conditions for the application of a molecule as a stabiliser, because the latter conditions include also a large number of parameters (compatibility with the polymer, molecular mobility, etc.).[1,2]

II. Photophysical processes in polyatomic molecules

The transformations of electronically excited molecular systems can occur with emission of photons (radiative transitions) or via a non-radiative pathway. The non-radiative routes to the decomposition of electronic states include non-radiative conversion processes in which the electronic excitation energy is converted into the vibration energy of the system without chemical transformations of the latter, autoionisation processes, electronic energy transfer and migration processes. All the processes enumerated are in the nature of physical processes involving the transformation of the electronic excitation energy and are referred to as photophysical. Apart from the photophysical routes to the transformation of molecular systems, there is also a possibility of photochemical routes, which lead to the formation of new chemical products. Photochemical processes are non-radiative.

The subdivision of the non-radiative pathways in the transformation of the electronically excited molecules into photophysical and photochemical is not always possible. In particular, it fails in molecules of many effective photostabilisers. Nevertheless, such subdivision must be used as the initial step in these cases too.

Very many studies[13–15] have been made on the characteristic features of photophysical processes in photostable molecules and on the development of their theory. Here we shall discuss briefly only the results which will be useful in the subsequent exposition.

Electronically excited molecular states can be classified[16] in terms of their multiplicity and orbital nature. The majority of molecules have a singlet ground state (S_0). In aromatic and heteroaromatic molecules the lowest excited singlet state is the $S_{\pi\pi^*}$ or $S_{n\pi^*}$ state. Triplet (T) states can also be of the $\pi\pi^*$ or $n\pi^*$ type. The lowest excited state of the molecules is a T state. There is a possibility of five types of relative dispositions of the singlet and triplet $\pi\pi^*$ and $n\pi^*$ states.[15,17]

The characteristic value of the rate constant for the radiative decomposition of $S_{\pi\pi^*}$ states (k_r^S) is $\sim 10^8-10^9$ s^{-1}, while that for the decomposition of the $S_{n\pi^*}$ state is $\sim 10^5-10^6$ s^{-1}. Since the $T-S$ transitions are forbidden as regards multiplicity, the rate constants k_r^T for the radiative decomposition of the T state are much smaller. In molecules without heavy atoms, k_r^T is $10^{-1}-10^2$ s^{-1} for $T_{\pi\pi^*}$ states and 10^3-10^4 s^{-1} for $T_{n\pi^*}$ states. The introduction of heavy atoms into the molecule leads to a significant (by several orders of magnitude) diminution of the lifetime of the T states. The above features are determined by the characteristics of the spin–orbital interaction in the molecule.[15,18–22]

There are three types of non-radiative conversion processes: internal conversion processes, which take place between states with the same multiplicity ($S-S$ or $T-T$), singlet–triplet ($S-T$) conversion processes, and triplet–singlet ($T-S$) conversion processes. We shall examine the characteristic rate constants for these processes.

The rate constants for internal conversion (k_{ic}) processes between excited states are very large ($\gtrsim 10^{11}$ s^{-1}). As a result of this, polyatomic molecules are seen to emit a luminescence with a high yield only from the lowest excited state of the given multiplicity (Kasha's rule[23]). On the other hand, it has been established for a large number of molecules that internal conversion S_1-S_0 processes make a small contribution to the decomposition of the lowest excited state,[24] i.e. that the constant k_{ic} for the S_1-S_0 conversion process is smaller than the constant k_r^S for the radiative decomposition of the S_1 states and the rate constant for the $S-T$ conversion (k_{ST}).

Theoretical study showed[25] that the above features of the internal conversion process are a consequence of the marked dependence of k_{ic} on the transition energy E_{if}. The dependence of k_{ic} on E_{if} is described approximately by the exponential law $\exp(-\alpha E_{if})$ with the parameter $\alpha \simeq 4-5$ eV^{-1}. For low values of $E_{if} \lesssim 1$ eV, the constant k_{ic} is $\gtrsim 10^{11}$ s^{-1} and exceeds the values of k_r^S and k_{ST}. Such values of E_{if} are characteristic of transitions between electronically excited states. For $E_{if} \gtrsim 2.5$ eV, the constant k_{ic} becomes smaller than k_r^S and k_{ST}. For a large number of polyatomic molecules, the energy difference between the S_1 and S_0 states satisfies this requirement and the internal conversion process is therefore unimportant in the degradation of the S_1 state. If the energy of the lowest excited state lies in the range 1.5–2.5 eV, the quantity k_{ic} is comparable to k_r^S and k_{ST} and in such molecules the S_1-S_0 internal conversion process may make an appreciable contribution. Experimental data confirming the foregoing can be found in a number of publications.[14,15,25–27]

The rate constant for the $S-T$ conversion between states of different nature ($\pi\pi^*$ and $n\pi^*$) reaches $\sim 10^{10}-10^{11}$ s^{-1} and the $S-T$ conversion process suppresses the fluorescence process.[15,21,22] The constant k_{ST} for the conversion between states of the same orbital nature is significantly lower and amounts to 10^6-10^9 s^{-1}. The $S-T$ conversion and fluorescence processes can compete in this instance.

The five types of relative positions of states of different orbital nature and with different multiplicities, mentioned above, and the characteristic features of the spin–orbital interaction and $S-T$ conversion processes serve as the basis of the luminescence-spectroscopic systematic treatment of molecules.[15,17]

Numerous studies have been devoted to the characteristics of $T-S$ conversion processes.[28–32] Of the general results, we shall mention here the energy gap law, in conformity with which the constants k_{TS} and k_{ic} diminish approximately exponentially with increase in the energy of the T state; here too the quantity α

amounts to approximately $4-5$ eV^{-1}. For many molecules in solid solutions, the constant k_{TS} is comparable to the rate constant for the radiative decomposition of the corresponding triplet state. (In liquid solutions this is not the case because different bimolecular processes involving the quenching of T states assume a significant role and the lifetime of such states falls sharply[33]).

In concluding this Section, it is important for our purpose to emphasise that the non-radiative degradation of the electronic excitation energy in the majority of photostable molecules takes place with a significant population of the triplet states, whose lifetimes are relatively long.

III. Initiation of non-radiative conversion processes by adiabatic photochemical reactions

Photochemical reactions are known to be capable of occurring via non-adiabatic or adiabatic mechanisms. The non-adiabatic reactions are similar to non-radiative conversion processes and reduce to a non-adiabatic transition between electronic states, one of which (the final state) is the state of the reaction products (for example, a predissociative state). In this case, the duration of the transition between the states is appreciably smaller than the reciprocal of the transition rate constant (i.e. the transition expectation time). The evolution of the system is therefore described with the aid of the usual kinetic scheme consisting of a series of independent competing processes, each of which is characterised by the corresponding rate constant.

Adiabatic photochemical reactions proceed without change in the electronic state of the system. They are usually described by the equation for the motion of the system on one potential surface from the minimum (region) for the initial system to the minimum (region) for the reaction products. The duration of the transition is in this case comparable to the reciprocal of the photoreaction rate constant. When an adiabatic photochemical reaction takes place, the probabilities of all the photophysical processes begin to depend on the reaction coordinate (x) and the usual kinetic treatment of the evolution of the system becomes inapplicable†. The dependence of the rate constants for the conversion processes on x becomes particularly significant.

We shall consider the possible cases where this dependence can be manifested most strongly. To make the system concrete, we shall have in mind initially S_1-S_0 internal conversion processes.[34]

The possibility of the occurrence of a photochemical reaction in the S_1 state during a period shorter than $\sim 10^{-8}$ s implies that the potential surface for this state either has no maximum, separating the initial state from the state of the reaction products, or that the maximum is small. In contrast to the S_1 state, in the S_0 state, the system is stable and the $U_0(x)$ potential surface has a deep minimum for certain equilibrium values of x. This minimum is separated by a high ($\gtrsim 1$ eV) potential barrier from the state of the reaction products in the electronic ground state. The form of the potential curves is illustrated schematically in Fig. 1*a* (continuous curves).

It is possible to distinguish another type of potential surface (Fig. 1*b*). If the reaction is impossible in the S_0 state, then that surface corresponds to repulsion. The possibility of the occurrence of the reaction in the excited state implies that the function $U_1(x)$ has a minimum corresponding to the reaction product. Isomerisation reactions (especially *cis–trans* isomerisation reactions), reactions), proton or hydrogen atom transfer reactions, etc. belong to the first type, while reactions involving the formation of excimers (an excited complex of two identical molecules) or exciplexes (an excited complex of different molecules) belong to the second type.

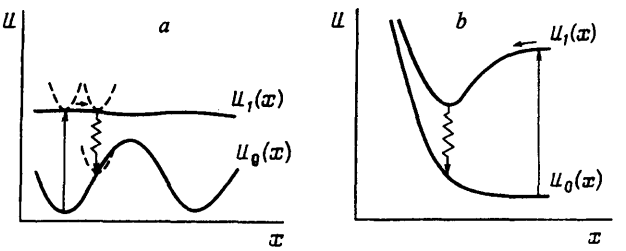


Figure 1. Schematic illustration of the potential surfaces for the isomerisation (*a*) and complex formation (*b*) reactions; the horizontal arrows indicate the movement of the system along the reaction coordinate.[34]

In the case of a condensed phase, subject to the condition that the vibrational relaxation rate constant exceeds the rate constants for all the remaining processes, the movement of the system along the reaction coordinate can be represented by a series of successive transitions through a series of quasi-equilibrium states. Their quasi-equilibrium is determined by the effect of the solvent on the molecular system—the finite orientational and translational relaxation time of the solvent (Fig. 1*a*, dashed curves). According to the theory of the condensed state put forward by Frenkel',[35] the lifetime of the system in each quasi-equilibrium state (the period between the jumps executed by solvent molecules from one state to another) exceeds $\sim 10^{-11}$ s and is much greater than the vibration period of the atoms in the system. The conversion process should therefore be regarded as one occurring between states of the system corresponding to the potential curves shown by dashed lines in Fig. 1*a*. This constitutes the difference between the mechanism of the conversion process occurring in the course of an adiabatic reaction and the mechanism of conversion in photostable systems, where the process takes place between two potential surfaces. The rate of the adiabatic photoreaction and its influence on photophysical processes and hence on the luminescence properties of the system depend on the characteristics of the medium (viscosity, intermolecular interaction, etc.).[36]

The significant decrease in the energy gap between the $U_0(x)$ and $U_1(x)$ potential curves leads to an increase in k_{ic}, which is greater the smaller the minimum difference $U_1(x)-U_0(x)$. Specific estimates can be made for certain reactions.

One of the widely occurring photoreactions with an adiabatic stage is the *cis–trans* isomerisation reaction, which can occur in the S_1 state of molecules having isolated or conjugated double bonds

† It is useful to note the analogy between this situation and the energy transfer process between diffusing molecules where the transfer rate constant depends on the distance between the moving molecules.

(stilbene and its derivatives, carbocyanine dyes, etc.).[36,37] In this case, the angle of rotation of the fragment about the double bond serves as the reaction coordinate. The activation energy $U°$ for this reaction in the S_0 state is 1–2 eV.[37] Neglecting the difference between the *cis*- and *trans*-isomers (1–3 kcal), the potential surface of the ground state can be described by the equation:

$$U_0(x) = \frac{U^0}{2}(1 - \cos 2x). \quad (1)$$

The $U_1(x)$ relation is known only for certain systems.[38] For our purposes, it is important to know only that the function $U_1(x)$ varies within narrow limits (~0.2 eV) and that the variation of the S_1-S_0 transition energy can be described satisfactorily by the expression:

$$E_{if} = E_{if}^0 - \frac{U^0}{2}(1 - \cos 2x), \quad (2)$$

where E_{if}^0 is the transition energy at $x = 0$. Using Eqn. (1) and (2) and the expressions for the rate constants k_{ic},[25] the $k_{ic}(x)$ relation has been calculated. The results are presented in Fig. 2. It follows from the data in this figure that k_{ic} increases with x to a greater extent the greater the parameter $U°$. The increase in k_{ic} becomes appreciable (by about two orders of magnitude) already in the initial stage of the reaction, where the angle of rotation of the fragment is ~45°. At $x = \pi/2$, k_{ic} reaches a maximum and diminishes on further increase in x.

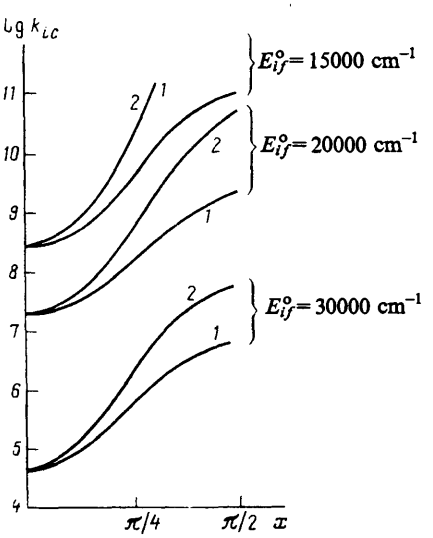


Figure 2. Dependence of k_{ic} on x for *cis–trans* isomerisation reactions with $U° = 8000$ cm^{-1} (curves *1*) and $U° = 12000$ cm^{-1} (curves *2*).[34]

If k_{ic} at $x = 0$ amounts to 10^6 s^{-1} ($E_{if}^0 \simeq 25000$ cm^{-1}), whereupon it is possible to neglect the contribution of the S_1-S_0 internal conversion process under conditions ruling out a photoreaction, then when a photoreaction occurs there is a possibility of the quenching of the fluorescence and the suppression of the $S-T$ conversion process. This effect is even more important for smaller values of E_{if}^0, whereupon the constant k_{ic} becomes $10^{10}-10^{11}$ s^{-1} during the photoreaction, which can lead to the suppression not only of the fluorescence and the $S-T$ conversion but also of the photoreaction itself. This conclusion has been confirmed experimentally[39,40] (see below).

As can be seen from Fig. 1*b*, in the case of complex formation reactions the maximum value of k_{ic} is attained at the minimum on the $U_1(x)$ curve. When excimers are formed, the decrease in the transition energy at this point reaches 5000–6000 cm^{-1}.[33] This change in the transition energy leads to a significant suppression of the fluorescence if E_{if}^0 for the isolated molecule does not exceed ~25000 cm^{-1}. It has been noted[34] that the mechanism of the initiation of the internal conversion process by the excimer formation reaction is the cause of the phenomenon of the concentration-induced quenching of the luminescence.

The initiation of the internal conversion process has been observed for proton transfer reactions.[40] For these reactions (as for any processes with a redistribution of the charge), processes involving the reorganisation (repolarisation) of the medium play a significant role. For such systems, we therefore find that, firstly, the influence of the polarity of the medium on the probability of the process is significant and, secondly, that there are difficulties in an unambiguous determination of the reaction coordinate. However, the general claim that the potential surfaces of the ground and excited states must approach one another for the initiation of the conversion process remains in force. This conclusion is consistent with experimental data, because the quenching of the S_1 states is most effective in systems where the proton acceptor is a weak base in the S_0 state, i.e. when the activation energy for the H^+ transfer process in this state is high.[40]

All that has been said above about the initiation of the internal conversion processes by adiabatic photoreactions refers directly also to the $S-T$ and $T-S$ conversion processes,[41,42] because the rate constants for the latter also increase with decrease in the energy gap. Furthermore, the change in the spin–orbital interaction (β_{s0}) as x varies is also significant for these processes. The increase in β_{s0} can be observed during reactions where fragments of the system are displaced from the plane[15] and on formation of complexes with a non-planar structure or complexes with molecules containing heavy atoms.[16] There is yet another cause of the initiation of the $S-T$ conversion process by a photoreaction: the change in the relative positions of the $\pi\pi^*$ and $n\pi^*$ states of different multiplicity during photoreactions.[41] Since the terms of the S and T states are usually of a similar form, the initiation of the $S-T$ conversion as a consequence of the change in the energy gap alone is relatively weak. In the case of the $T-S$ conversion, the occurrence of the latter is significantly reflected in the phosphorescence yield, because $k_r^T \simeq k_{TS}$ even in photostable systems.

The equation for the probability of finding the system at time t in the initial electronic state at the point x on the reaction coordinate is fairly simple and at the same time makes it possible to analyse the behaviour of the system. It assumes the form:[42,43]

$$\frac{\partial W_S}{\partial t} = D\frac{\partial^2 W_S}{\partial x^2} - v\frac{\partial W_S}{\partial x} - [k_r^S + k_{ic}(x)]\,W_S. \quad (3)$$

This follows from the more general Focker–Planck equation. Eqn. (3) has been formulated for the initiation of the S_1-S_0 internal conversion process. The parameter D characterises the diffusional movement of the system along the S_1 surface and v is the velocity of the system along the reaction coordinate under the influence of the force determined by the dependence of the S_1 term value on x, which

is assumed in this instance to be linear. It has been suggested that the rate constant for the radiative decomposition of the S_1 state is independent of x and $S-T$ conversion processes may be neglected. [For an unchanged value of k_{ST}, Eqn. (3) retains its form, but k_r^S should be understood as the sum of the rate constants for the radiative decomposition of the S_1 state and for decomposition as a consequence of the $S-T$ conversion.]

We shall consider certain special cases. Suppose that $D = 0$ and that the system is in the initial instant at the point $x = 0$ [$W_S(x, 0) = \delta(x)$] and begins to move in the positive direction of the x axis along the sloping term of the S_1 state. After the attainment of the point $x = L$, the photoreaction is assumed to be completed (at this point the potential energy increases sharply). The rate of movement of the system along the S_1 term is linked to the reaction time by the relation $\tau_R = Lv^{-1} = k_R^{-1}$. The population of the S_1 state

$$W_S(t) = \int_0^L W_S(x, t)\,dx \quad \text{at} \quad t \leqslant \tau_R ,$$

is given by the expression:

$$W_S(t) = \exp[-k_r^S t - v^{-1}k_{ic}(vt)],$$

where

$$k_{ic}(x) = \int_0^x k_{ic}(x')\,dx'.$$

The law governing the decomposition of the S_1 state is not exponential. For $t > \tau_R$, the system is in the S_1 state of the photoproduct and its further evolution is described by the usual law: $Q_R^S exp\text{-}\{[k_{ic}(L) + k_r^S]t\}$, where Q_R^S is the yield of the photoproduct in the S_1 state and $k_{ic}(L)$ is the constant for the internal conversion of this state. If during the movement along the S_1 term the energy diminishes by an amount ΔE, then the dependence of k_{ic} on x can be represented in the form $k_{ic}(x) = k_{ic}^\circ \exp(\alpha \Delta E x L^{-1})$, where k_{ic}° is the conversion constant in the initial system (for $x = 0$) and α is a coefficient in the exponential dependence of k_{ic} on the transition energy (see Section II).

The quantum yields of the fluorescence (Q_r), internal conversion (Q_{ic}), and the photoproduct (Q_R^S) are given by the expressions

$$Q_r = e^a b^b [\Gamma(-b, a) - \Gamma(-b, ae^A)],$$
$$Q_{ic} = e^a a^b [\Gamma(1-b, a) - \Gamma(1-b, ae^A)],$$
$$Q_R^S = 1 - Q_r - Q_{ic}, \qquad (4)$$

where $a = k_{ic}^\circ Z^{-1}$, $b = k_r^S Z^{-1}$, $Z = Ak_R$, $A = \alpha\Delta E$, and $\Gamma(x,y)$ is an incomplete gamma-function. The radiation and photoproduct conversion quantum yields are calculated from the usual expressions with $k_{ic} = k_{ic}^\circ \exp(\alpha \Delta E)$.

Fig. 3 presents the dependence of Q_r, Q_{ic}, and Q_R^S on the parameter A. Evidently in the range of values of A where $k_{ic}(x)$ exceeds k_r^S and k_R (for $A \geqslant 5$ or $\Delta E \gtrsim 1$ eV), the internal conversion suppresses not only the fluorescence process but also the very photoreaction which has accelerated the internal conversion.

Fig. 4 presents the dependence of Q_{ic} on D for the case where the energy of the S term is independent of x, $v = 0$, and the movement of the system along the term is diffusional in character. The initial condition has the same form as above, while $k_{ic}(x)$ is given by the expression $k_{ic}(x) = k_{ic}\exp(c \sin^2 x)$, which corresponds to Eqn. (1) for the energy of the S_0 term. The boundary condition $(\partial W_S/\partial x)_{x=\pm\pi/2} = 0$ models the situation where the photochemical reaction cannot be completed as a consquence of steric hindrance [the function $U_1(x)$ at these points becomes infinite]. The boundary condition $[W_S(x,t)]_{x=\pm\pi/2} = 0$ describes the situation where the system undergoes instantaneous photochemical decomposition after the attainment of the boundaries. (One can then introduce the reaction rate constant $k_R \simeq D$.[42]) The value of the parameter $c = \ln 10^3$ employed corresponds to the value of U° in Eqn. (2), which is $\sim$1.5 eV. Evidently even when the reaction can occur under conditions such that it cannot reach completion, the internal conversion process is rapidly accelerated, which can lead to the suppression of both fluorescence and the photoreaction itself.

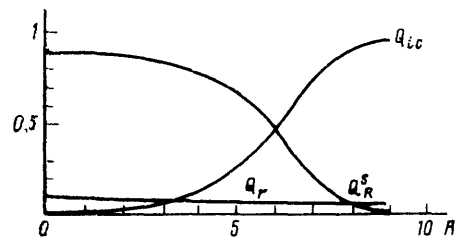


Figure 3. Dependence of Q_r, Q_{ic}, and Q_R^S on the parameter $A = \alpha\Delta E$; $k_r^S = 1$, $k_{ic}^\circ = 1$, $k_R = 10$.

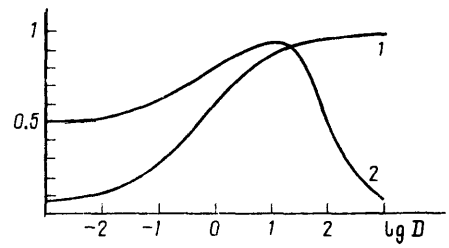


Figure 4. Dependence of Q_{ic} on D for a system with a *cis–trans* isomerisation reaction: *1*, boundary condition $(\partial W_S/\partial x)_{x=\pm\pi/2} = 0$, $k_r^S = 1$, $k_{ic}^\circ = 0.1$; *2*, boundary condition $[W_S(x,t)]_{x=\pm\pi/2} = 0$, $k_r^S = 1$, $k_{ic}^\circ = 1$.

Two main conclusions follow from the foregoing. (1) A significant initiation of the internal conversion process is observed when the minimum energy gap between the S_1 and S_0 terms does not exceed 2–2.5 eV. (2) Provided that $k_{ic}(x) \gg k_R$, $k_{ic}(x) \gg k_R^s$ for $0 < x < L$, and $k_r^S \simeq k_R$, when the first condition is fulfilled the internal conversion process leads not only to the quenching of the fluorescence but also to the suppression of the photoreaction. In the range of values $k_R \gg k_r^S$ and $k_{ic}(x) \ll k_R$, the evolution of the excited state is determined by the ratio of the quantities k_r^S and k_{ic} for the photoproduct. The latter conclusion holds also for other types of conversion.[42]

It was suggested above that the rate constant for the vibrational relaxation significantly exceeds the rate constants for other processes involved in the evolution of the system and that the movement of

the system along the reaction coordinate is limited by the relaxation of the solvent. In certain cases, this condition may break down. Thus, in the concluding stage of the reaction involving the formation of excimers or exciplexes, where there are no solvent molecules between the reacting molecules, the mutual approach of the reactants is not limited by the relaxation of the solvent. In this situation, there is a possibility of the formation of the reaction product in a highly excited vibrational state, as happens in the gas phase. A similar situation can occur also for other reactions.

This case has been analysed in detail.[44] It has been shown that the internal conversion process can compete with the vibrational relaxation process, provided that the terms of the ground and S_1 states intersect in the region of the energies of the vibrational states of the reaction product. The conversion process can occur with an appreciable probability even from states of the continuous spectrum of the collision complex, provided that the point of intersection of the surfaces is located in the classically accessible region or in its vicinity. For H atom and H^+ transfer reactions, the probability of the conversion process is high also in the sub-barrier region.

The position of the point of intersection of the terms for the excimer formation processes is determined by the oscillator strength f of the S_1-S_0 transition. It has been shown[44] that the quenching of the excimers from vibrationally excited states is possible if $f \gtrsim 0.5$, which is characteristic of many dye molecules which undergo concentration-induced quenching of their luminescence. For exciplexes with a significant charge transfer contribution, such a situation is more probable the higher the electron affinity of one of the reactants and the lower the ionisation potential of the other. The latter makes it possible to understand the characteristic features of the quenching of singlet oxygen by electron donors, in particular the observed increase in the quenching constant with decrease in the ionisation potential of the quenching agent.[5,6]

In concluding this Section, we may note that, in the case of systems with sensitised conversion processes, on the one hand, there is a significant decrease in the lifetime of the excited states and, on the other, the pathway leading to the degradation of the energy changes: as a consequence of the acceleration of the internal conversion process, the degradation of the excitation energy takes place without the triplet states being populated or with a significant decrease in their population.

IV. Photophysical properties of effective photostabilisers

Using the results described above, here we shall discuss the question which photophysical properties effective photostabilisers should possess in addition to the requirements specified in the Introduction.[1,2,7–12] It is not difficult to satisfy the requirements set out above using π-electron and especially aromatic (heteroaromatic) molecules. However, this is not sufficient.[45]

Indeed the photostabiliser molecule in an excited state can itself undergo irreversible phototransformations. It would appear that, in order to eliminate this undesirable effect, it should be sufficient to employ molecules exhibiting photostability in the lowest S and T states, which has been observed for a large number of π-electron molecules. However, it is important to take into account the following factor. The molecule in the lowest relatively long-lived T state can absorb a second light quantum and undergo a transition to highly excited T states.[46] In these states, all molecules without exception are reactive,[46,47] decomposing into fragments or ionising (auto-ionising). Although the probability of two-quantum $T-T$ excitation is low, the efficiency of the action of photostabilisers depends significantly on the contribution of these excitations, because one is dealing with the long term behaviour of this system.

The number of molecules excited to the highest triplet states increases with increase in the quantum yield of the lowest triplet states and their lifetime. An additional requirement which must be met by the properties of effective photostabilisers is therefore that the populations and lifetime of the lowest T states of the molecules should be as small as possible. We shall discuss different cases from this standpoint.

We shall consider initially molecules which are photostable in the lowest electronically excited state. In the absence of intermolecular $T-T$ energy transfer processes, the population of the lowest T state is determined by the relation between the constants for the radiative decomposition of the S_1 state and the value of k_{ST}, because in most cases S_1-S_0 conversion processes will not play a significant role. If the rate of the $S-T$ conversion process is determined by the transitions between the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ or between the $S_{n\pi^*}$ and $T_{\pi\pi^*}$ states (molecules belonging to luminescence spectroscopic types II–IV [15,17]) or if the molecule contains heavy atoms, then $k_{ST} \gg k_r^S$ [16] and the quantum yield of the T state is almost unity. For molecules belonging to luminescence spectroscopic types I and V, the $S-T$ conversion process takes place between states of the same orbital nature and $k_r^S \simeq k_{ST}$.[15] Only for isolated dye molecules and effective phosphors is the relation $k_r^S \gg k_{ST}$ observed. It arises from the characteristic features of the disposition of the excited $T_{\pi\pi^*}$ states relative to the $S_{\pi\pi^*}$ state and the spin–orbital interaction selection rules.[16,48] Such molecules have a high fluorescence quantum yield and their photostabilising efficiency is frequently also high, but they cannot always be used. On the other hand, for most photostable molecules the yield of the T states cannot be very low, especially since the latter can arise also via the $T-T$ energy transfer route.

The lifetime of the $T_{\pi\pi^*}$ states of molecules without heavy atoms in solid solutions (and not only at low temperatures)[49] is very long. Photostable molecules with the lowest $T_{\pi\pi^*}$ state are therefore not very effective photostabilisers and can in fact function as photosensitisers. The $T_{n\pi^*}$ states are short-lived and the $T-T$ absorption processes are relatively unlikely for such states.[46] However, the majority of molecules with the lowest $T_{n\pi^*}$ state are reactive. In particular, they participate in photodehydrogenation reactions.[36]

The lifetime of the $T_{\pi\pi^*}$ states may be sharply reduced (by 3–4 orders of magnitude) after the introduction of heavy atoms into the molecule. It changes in inverse proportion to the fourth power of the effective charge on the heavy atom. Many organometallic compounds are therefore good photostabilisers.[1,2] (Unfortunately, some of them behave as catalysts of oxidation reactions.[50])

As is already clear from the foregoing, there exists yet another possibility of reducing the lifetime of the T states with the simultaneous decrease in their population, which is associated with the initiation of S_1-S_0 and $T-S$ conversion processes by reversible adiabatic photoreactions.

We shall consider the behaviour of a system with potential surfaces ensuring the occurrence of a reversible photoreaction in S and T states (Fig. 5). Neglecting diffusion, the population of the S_1 state $W_S(x,t)$ is specified by an equation which is analogous to Eqn. (3) for $D = 0$:

$$\frac{\partial W_S}{\partial t} = -v\frac{\partial W_S}{\partial x} - [k_r^S + k_{ST} + k_{ic}(x)]\,W_S. \qquad (5)$$

We shall assume that the constants k_r^S and k_{ST} are independent of x, that $k_{ic}(x)$ increases exponentially with increase in x, and that the initial condition is $W_S(x,0) = \delta(x)$. Using the above results, one can write the following expression for the quantum yield of the T state:

$$Q_T = k_{ST} I_1 + Q_R^S k_{ST} [k_r^S + k_{ST} + k_{ic}(L)]^{-1}, \quad (6)$$

where Q_R^S is the quantum yield of the photoproduct in the S_1 state, amounting to $1-(k_r^S + k_{ST})I_1 - I_2$, I_1 and I_2 being defined by the same expressions as Q_r and Q_{ic} respectively in Eqn. (4). The quantity $b = (k_{ST} + k_r^S)Z^{-1}$ is overdetermined.

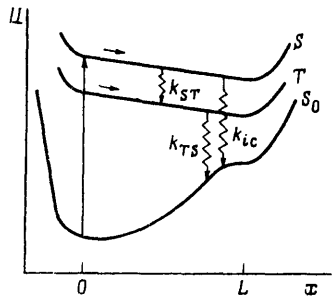


Figure 5. Schematic illustration of the terms for a molecular system with a reversible photochemical reaction; the horizontal arrows indicate the movement of the system along the reaction coordinate.[45]

Table 1. Dependence of the quantum yield of T states on the parameters $A = \alpha\Delta E$ and $k_R = v/L$ [$k_{ic}^0 = 0.1$, $k_{ic}(x) = k_{ic}^0 \exp(AxL^{-1})$, $k_{ST} = 0.5$, $k_r^S = 0.4$].

A	k_R					
	0	10^{-1}	1	10	10^2	10^3
4	0.5	0.435	0.269	0.107	0.08	0.077
6	0.5	0.424	0.220	0.049	0.016	0.012
8	0.5	0.412	0.188	0.037	0.006	0.002

Table 1 presents the quantum yields of the triplet state for different values of the parameters A and k_R. It is seen from these data that the yield of the T state diminishes sharply with increase in k_R and tends to the limiting value $k_{ST}[k_{ST} + k_r^S + k_{ic}(L)]^{-1}$ at $k_R \to \infty$, which is equal to the yield of the triplets in the photoproduct. The decrease in Q_T is more notable the higher the value of the parameter A, i.e. the greater the difference between the energies of the S_1-S_0 transition at the points $x = 0$ and $x = L$.

We shall now consider the influence of the initiation of $T-S$ conversion processes on the probability of secondary reactions. The population of the lowest T state is given by the equation:

$$\frac{\partial W_T}{\partial t} = -v\frac{\partial W_T}{\partial x} - [k_r^T + k + k_{TS}(x)]\, W_T, \quad (7)$$

where k is the rate of a secondary reaction [for example, the rate of $T-T$ absorption or transfer of energy to reactive molecules (in particular O_2)]. Subject to the initial condition $W_T(x,0) = \delta(x)$ and the exponential dependence of k_{TS} on x: $k_{TS} = K_{TS}^0 \exp(AxL^{-1})$, and for $k \ll k_r^T + k_{TS}^0$, one can find the following expression for the relation for the yield of the secondary reactions to its yield corresponding to $A = 0$:

$$\overline{Q} = (k_r^T + k_{TS}^0) I_1 + \frac{k_r^T + k_{TS}^0}{k_r^T + k_{TS}^0 e^A} Q_R^T . \quad (8)$$

The quantum yields of the photoproducts in the T state, Q_R^T and I_1, are calculated from formulae similar to those presented above. The dependence of $\overline{Q}$ on the rate of an adiabatic photoreaction is illustrated in Fig. 6. Evidently, for realistic values of the parameter $A = 4-8$ ($\Delta E = 1-2$ eV), we have $\overline{Q} < 10^{-1}$, provided that k_R exceeds the sum $k_r^T + k_{TS}^0$. A significant decrease in $\overline{Q}$ is observed even when Q_R^T is very low. $\overline{Q}$ diminishes to an even greater extent when account is taken of the effect of the occurrence of the S_1-S_0 internal conversion both as a result of the decrease in the yield of the T state and because the point from which the system begins to move along the T state surface may be one with a coordinate $x > 0$ where k_{TS} is greater than k_{TS}^0. The initiation of S_1-S_0 conversion processes suppresses the unlikely but possible two-quantum reactions in S states.

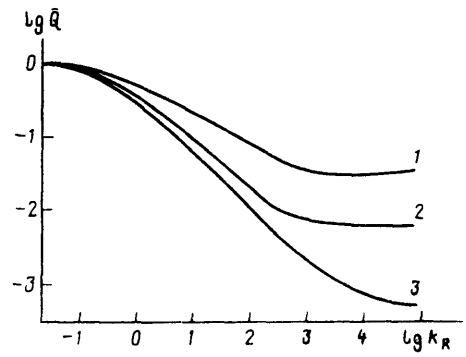


Figure 6. Dependence of $\overline{Q}$ on k_R for $k_r^T = k_{TS}^0 = 1$: *1*, $A = 4$; *2*, $A = 6$; *3*, $A = 8$.[45]

Similar results have been obtained also for more complex models of potential surfaces, in particular for the *cis–trans* isomerisation reaction for which the maximum values of $k_{ic}(x)$ and $k_{TS}(x)$ correspond not to the reaction product but to an intermediate region and movement along the term of the excited state is diffusional.

Thus in the case of the most effective photostabilisers the population of the T states and (or) their lifetime should be the smallest possible. The fulfilment of one of the conditions specified may be sufficient. The compositions formulated supplement the generally known requirements[1,2] imposed on photostabilisers. When molecules with a fluorescence quantum yield equal or close to unity are used, the first condition holds, for molecules with heavy atoms the second condition holds, while both conditions can be fulfilled in the case of molecules for which the S_1-S_0 and $T-S_0$ conversion processes are initiated by reversible photochemical reactions. Clearly the most

characteristic feature of systems of the latter type is the absence of an appreciable luminescence yield.

We emphasise that the initiation of the conversion processes by an adiabatic photoreaction is important and not the actual occurrence of the photoreaction itself.

The occurrence in the molecular system of luminescence with a large Stokes shift, which may be a consequence (although not always; see, for example, Frank-Kamenetskii and Lukashin[51]) of an adiabatic photochemical reaction, is not a sufficient condition for using the system as an effective photostabiliser.

The above requirements and the ways in which they are met hold also for intrinsically photostable polymers, since the inclusion in the polymer chain of fragments with the photophysical properties listed above increases its photostability.

The experimental data for the photostabilising efficiency of molecular systems will be considered below on the basis of the ideas described above.

V. Principal structural types of photostabiliser molecules

The agreement between the ideas set out above and the available experimental data will be demonstrated in this Section in relation to the most typical examples of systems possessing photostabilising properties. The systematic treatment of these data is based on the photophysical characteristics of photostabiliser molecules and, in particular, on the type of adiabatic photoreaction accelerating the non-radiative conversion.

1. Systems with an intramolecular hydrogen bond (IAHB)

Until recently, photostabilisers of this type have found the greatest practical application in thermoplastic, thermoelastoplastic, and reactoplastic materials[52] and they are being manufactured on a large scale by a number of undertakings in the USSR and abroad.[53–55] It is of interest to trace the development in the course of time of ideas about the mechanism of the action of photostabilisers with an intramolecular hydrogen bond.

A high capacity to absorb UV light in the range 300–400 nm is characteristic of aromatic derivatives with an intramolecular hydrogen bond. In the first publications devoted to the study of such stabilisers (derivatives of benzophenone, benzotriazole, and salicylic acid), their stabilising effect was attributed[56] to their ability to absorb UV light (shielding effect). From the middle 1940's until the beginning of the 1960's, this was the only explanation of the photostabilising capacity of such substances. However, it had long been noted that the proposed mechanism is unable to account fully for the observed protecting effect. For example, a decrease in the molar extinction coefficient ε of phenyl salicylate derivatives leads to an increase in the photoprotecting effect.[57] It was also not understood why certain structurally similar substances with an intermolecular hydrogen bond and with a high extinction coefficient ε (for example, 2-hydroxyphenyl-1,2,4-triazole) do not exhibit a photostabilising effect.[58]

Later the view was expressed in a number of studies[59–62] that, together with the absorption of UV light, UV absorbers can quench excited polymer centres or impurities which are always present in real industrial polymers. The absorption of light in the range 280–400 nm in polymers such as polyolefins (PO), poly(vinyl chloride) (PVC), and polystyrene (PS) is associated with the presence in these substances of oxidation products, variable-valence metallic impurities (for example, catalyst residues), and polycyclic hydrocarbons adsorbed from the atmosphere.[63,64] Furthermore, in the presence of oxygen in polymers [polyethylene (PE), polypropylene (PP), etc.], complexes are formed whose absorption spectra have undergone a bathochromic shift compared with the spectrum of the [pure] polymer owing to the appearance of a charge-transfer band.[65–67] The oxygen molecule is an effective quenching agent for excited states[58] but it does not exhibit photostabilising effects in polymers. On the contrary, it accelerates the photodecomposition of many polymeric materials.[68]

In 1966–1968, Pivovarov and Lukovnikov and co-workers[7–10] and later George[69,70] published a series of studies which significantly altered the ideas about the mechanism of the action of UV absorbers with an intramolecular hydrogen bond. It was shown convincingly in relation to polypropylene that typical UV absorbers such as *p*-(*t*-butyl)phenyl salicylate, 2-(2-hydroxy-5-methylphenyl)benzotriazole, and 2-hydroxy-4-octyloxybenzophenone effectively quenched the luminescence of the polymer with energy transfer to the stabiliser. Depending on the polymer irradiation conditions, the cross-section of the specimens, the exposure time, and the type of stabiliser, the contributions of the shielding and quenching effects may vary and quenching can predominate.[8] Furthermore, after prolonged exposure of the polymer specimens, the quenching of the photochemical oxidation products (carbonyl groups) may become important.[70]

The rules specified above, according to which the stabiliser must absorb light energy to the maximum extent in the region where the polymer absorbs and in the region of its luminescence, were formulated in these studies.[9] In polymers which luminesce in their initial state (before irradiation), the greatest protecting efficiency may be achieved by using mixtures of stabilisers one of which ensures the protection of the polymer molecules and the other must deactivate the oxidative degradation products.[70,71] The validity of these conclusions was confirmed in subsequent investigations.[72–74]

Until recently there was no unanimous view in the literature concerning the role of the intramolecular hydrogen bond in the appearance of the photostabilising effect. The stabilising properties of UV absorbers have been attributed[75–77] to the presence in their structure of a quasi-aromatic ring with a strong hydrogen bond in the ground state of the molecule. However, the estimate of the efficiency of these compounds based on the strength of the intramolecular hydrogen bond[78,79] reflects only the shielding capacity of the stabiliser (the intensity of the absorption band in the range 310–370 nm increases with increase in the energy of the intramolecular hydrogen bond) and does not indicate the practical possibility of using the compound as a photostabiliser. On the other hand, if account is taken of the fact that the energy of the intramolecular hydrogen bond changes when the molecule passes to an excited state and the bond frequently breaks,[80] the possibility of correlation between the strength of the intramolecular hydrogen bond and the stabilising efficiency looks problematical.

It is essential to note yet another approach to the explanation of the mechanism of the deactivation of energy by UV absorbers with intramolecular hydrogen bonds. It has been suggested[81,82] that the most effective stabilisers should be aromatic compounds with an intramolecular hydrogen bond which fluoresce with an anomalously large Stokes shift (derivatives of 2-hydroxyphenylbenzotriazole and 2-hydroxyphenylbenzoxazole) but no experimental data confirming the high efficiency of these compounds are quoted. On the other hand, it is known from literature data[58] that 2-hydroxyphenylbenzoxazole is not efficient as a photostabiliser. Furthermore, in

highly dilute solutions in hydrocarbons, 2-hydroxy-derivatives of benzotriazole exhibit a weak fluorescence with a normal Stokes shift[83] and λ_{max} = 25 000 cm^{-1}, while the glow of this compound observed by Betin[82] is due to the crystalline phase (λ_{max} = 15 000 cm^{-1}). The glow of the crystalline phase at λ_{max} = 22 000 cm^{-1}, erroneously attributed to fluorescence with an anomalously large Stokes shift, has been observed[84] for 2-hydroxyphenylbenzoxazole whose crystals fluoresce with λ_{max} = 21 500 cm^{-1}.[85]

A significant step towards the understanding of the problem under discussion was made in a number of studies[83,86–89] carried out in 1979–1986 using luminescence-spectroscopic methods. The authors analysed the results of investigations of the photostabilising efficiencies of compounds with an intramolecular hydrogen bond on the basis of modern ideas concerning the nature of non-radiative conversion processes in polyatomic molecules, in particular, taking into account the effect of the initiation of these processes by adiabatic photoreactions.[89,90] *It was concluded that molecules with an intramolecular hydrogen bond, for which the lifetime and population of the triplet state are low, exhibit a high photostabilising efficiency as a consequence of the initiation of the S_1-S_0 and $T-S$ conversion processes by reversible intramolecular proton transfer reactions.* This effect leads to the suppression of secondary reactions of T states and ensures a high photostabilising efficiency of systems of this kind.

In conclusion of this Section, we may note that during the last ten years no information has appeared in the literature concerning new types of photostabilisers with an intramolecular hydrogen bond. Benzotriazole[91–96] and benzophenone[97–101] derivatives, modified by different substituents in order to diminish their migration from the polymer and to improve their toxicological properties, are still being patented and recommended for use. A fairly complete survey of the methods of synthesis and applications of different derivatives of 2-hydroxyphenylbenzotriazole has been published.[102]

2. Molecules in which there is a possibility of the *cis–trans* isomerisation reaction

The *cis–trans* isomerisation photoreaction is possible in molecules of azo-compounds, azomethines, stilbenes, chalcones, etc. The rotation of the molecular fragments in the electronically excited state is about the –N=N–, –N=C–, and –C=C– bonds. The reaction can take place both in the liquid phase and in solid polymer matrices.[103] Data on the mechanism of the *cis–trans* isomerisation reaction can be found in a number of communications.[104–107]

A characteristic feature of the majority of arylazo-compounds is the absence of luminescence in liquid and solid solutions and in polymer matrices (alkylamino- and dialkylamino-azobenzenes luminesce weakly in solid matrices at 77 K[108]). Very intense fluorescence has been observed only in *o*-hydroxyarylazo-compounds which tend to undergo the azo-hydrazone tautomerism. The fluorescence has been attributed to the hydrazo-form,[109] which is incapable of *cis–trans* isomerisation.

Among azo-compounds there are dyes of virtually every colour ranging from yellow to black. Depending on the nature of the substituent in the aromatic ring, the photostability and photochemical activity of azo-compounds can vary significantly—from the sensitisation of photochemical reactions to the pronounced photostabilisation effect. It has been observed experimentally that, as a rule, the fluorescent azo-dyes are sensitisers of the photodegradation of polymeric materials.[1] On the other hand, in the majority of photostable dyes, which are capable of increasing the photostability of the polymer (polyamide fabrics), there is no luminescence or it is observed to occur with a very low quantum yield.[110,111] The results of studies on the use of arylazo-compounds as photostabilisers of block-copolymers of isoprene with styrene (IST-30) have been published.[112–114] It has been shown that many azo-compounds, particularly those with amino- or hydroxy-groups in the *para*-position in the benzene ring, as well as nitro- or phenylazo-groups in the 4-position relative to the azo-group are more effective photostabilisers of polydienes than the photostabiliser Tinuvin P used in industry. On the other hand, compounds containing a hydroxy-group in the *ortho*-position relative to the azo-group are relatively ineffective as photostabilisers. The reason for the low efficiency of *ortho*-substituted derivatives and the high efficiency of the *para*-substituted derivatives is that in the series of derivatives of azo-benzene, *para*-derivatives do not luminesce as a consequence of the effective non-radiative deactivation initiated by the *cis–trans* isomerisation reaction, while *ortho*-hydroxy-derivatives do exhibit a luminescence with a high quantum yield[115] and therefore their excited states have a relatively long lifetime.

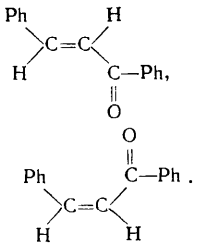
Although the wide-scale practical application of arylazo-compounds as photostabilisers of polymeric materials is limited because of their intrinsic colour (they are unsuitable for the manufacture of white or colourless articles from polymers), they have been recommended for use in polyolefins and in PVC,[116,117] in vulcanised butyl rubbers dyed to give light colour shades,[118] in linear polyesters,[119] and in styrene and rubber block-copolymers.[120] They exhibit a high stabilising effect in polyamides.[121]

Compounds with C=N bonds, namely benazine,[122] furfurylazine,[123] salicylazine,[124] and tetrazine,[125] have already been known for many years as photostabilisers of polymers of different types. There is a high probability of deactivation processes involving the non-rigid molecules of these compounds, which are capable of *cis–trans* isomerisation. Thus benazine (dibenzylideneazine) Ph–CH=N–N=CH–Ph does not luminesce either as a crystal or in solution (at room temperature and at 77 K).[85] Benzylideneaniline and many similar azomethines having different substituents in the benzene ring behave similarly. The effective non-radiative conversion in these systems is associated with the change in the steric structure in the excited state.[126,127] Molecules with a rigid structure, where the C=N group is incorporated in a ring (for example, phenylbenzimidazole) or having rings with intramolecular hydrogen bonds (salicylideneanilines, *o*-tosylaminobenzaldehydes), become luminescent.[128–130] In this case the *cis–trans* isomerisation reaction is impossible or is greatly hindered and the photostabilising properties of the molecules are impaired.

Diarylethylenes (stilbenes) are typical representatives of systems in which *cis–trans* isomerisation takes place. There exists an extensive literature on studies of the luminescence-spectroscopic properties of these compounds and of the isomerisation reaction mechanism.[85,131–138] As a rule, molecules in the *trans*-form fluoresce, while the *cis*-isomers hardly fluoresce. Apparently the difference in the behaviour of the *cis*- and *trans*-forms limits the applicability of stilbenes as stabilisers.

The molecules of indigoid and thioindigoid dyes having a central C=C bond also undergo *cis–trans* isomerisation. A high photostability and ability to increase the resistance to light-induced ageing of dyed materials are characteristic of these compounds.[139,140] It has been shown[141] that only the *trans*-isomers fluoresce, while the *cis*-isomers do not fluoresce and do not phosphoresce. The luminescence-spectroscopic properties of indigoid dyes have been surveyed.[115,142]

The *cis—trans* isomerisation reaction is characteristic also of α,β-unsaturated ketones with aromatic rings (chalcones). The isomerism of these compounds is determined by the relative positions of the substituents in relation to the C=C bond of the vinylene group:



These compounds do not luminesce, like other compounds with a non-rigid structure,[142] because the conversion processes occurring in them are accelerated by *cis—trans* isomerisation reactions. They have been recommended as effective photostabilisers.[143,144]

Thus many systems in which conversion processes are initiated by the *cis—trans* isomerisation reaction are effective photostabilisers.

3. Systems in which there is a possibility of the formation of excimers and exciplexes

As stated in Section IV, the non-radiative conversion processes can be accelerated on formation of excimers and exciplexes. Some data on the properties of these systems can be found in a number of communications.[31,145,146] Apart from intermolecular excimers and exciplexes, it has become usual to refer also to intramolecular ones. The formation of the latter is attributed to a rearrangement of the structure of the molecule in the excited state such that the different fragments undergo a significant change in their positions in space and the distance between them diminishes. Examples of the formation of intramolecular excimers have been published.[147–149]

Among systems used as photostabilisers in which there is a possibility of the formation of excimers (exciplexes), mention should be made of derivatives of acrylic acid,[150–152] benzylidenemalonates,[56] phenyl benzoates and carboxylic acid amides,[153] and aromatic derivatives of phosphoric acid.[154] The mechanism of the photoprotecting action of these compounds was not understood until attention was turned to the relation between the stabilising properties of molecules and the initiation of non-radiative conversion by reversible photoreactions.[45]

A detailed analysis of the mechanism of conversion for aromatic derivatives of phosphoric acid has been carried out[155] on the basis of quantum-chemical calculations by the CNDO/2 method.[156] Compounds having the structure Ph—X—PO(Y—Ph)—X—Ph, where X = Y = O, X = Y = NH, and X = O, Y = NH, were investigated. It was established that, in the equilibrium configuration of the excited S_1 state, these molecules have a sandwich structure with an almost parallel disposition of benzene rings, as in the excimers of benzene[157] and polystyrene.[158] This entails a decrease in the difference between the energies of the S_1 and S_0 states, the acceleration of the internal conversion process, and a decrease in the population of the T states. Furthermore, the non-planar structure of these systems and the presence of the central heavy P atoms ensure a high rate of $T—S$ conversion processes. Accordingly, aromatic derivatives of phosphoric acid do not luminesce in solutions either at room temperature or at 77 K and exhibit very pronounced photostabilising properties.[154]

A similar conversion mechanism operates in other known photostabilisers which do not contain an intramolecular hydrogen bond in their structure (oxanilides, benzamides, benzoates, and acrylate esters). Their steric rearrangement in the excited state is sufficiently rapid (over a period $\lesssim 10^{-11}$ s[159]) to ensure conditions for the initiation of conversion processes.

The unusual behaviour of phenyl benzoates in polymers has for a long time attracted attention.[2] The stabilising capacity of these systems has been traditionally attributed to the Fries photorearrange-ment,[160] which results in the formation of 2-hydroxybenzophenones which protect the polymer as molecules with an intramolecular hydrogen bond. However, this explanation proved to be over-simplified because it has been shown[57] and then confirmed[161] that phenyl benzoates are themselves photostabilisers. An even more direct proof of this postulate was obtained in a study[162] where it was shown that chloro-substituted phenyl benzoates, in which the Fries rearrangement is impossible, exhibit a stronger photoprotecting effect than compounds in which such rearrangement is possible.[125] The mechanism of such conversion in phenyl benzoate has been examined in an investigation[163] where it was shown that the absence of luminescence and the high photostabilising efficiency of this compound are associated with the initiation of conversion processes as a consequence of a conformational rearrangement of the type involving the formation of an intramolecular excimer.

Aromatic derivatives of acrylic acid, investigated by luminescence spectroscopic methods,[164] also have a low luminescence yield as a consequence of sensitised conversion processes. Since in addition they do not undergo irreversible photoreactions,[165] their photostabilising efficiency is high.

Diaryloxamides,[166–171] having the general formula $R^1—Ph—NH—CO—CO—NH—Ph—R^2$ and exhibiting a high stabilising efficiency in polymer-containing coatings, varnishes, and polycarbonates, have similar properties. The conversion mechanism under discussion operates also in the recommended derivatives of benzoic and benzacrylic acids[170–174] and in benzoylmethane[175–177] (stabilisers of butadiene rubber and cosmetic preparations).

There are fairly numerous literature data on the quenching of the excited states of polymers by electron-donating complex-forming agents. Thus it is well known that the formation of complexes between amines and the carbonyl groups of polymeric molecules entails the initiation of conversion processes and the quenching of excited states in exciplexes.[145] Other compounds having a relatively low ionisation potential behave similarly.[145]

The question of the deactivation of singlet oxygen molecules occupies an important place in the problem of the photostabilisation of polymers. They arise as a result of energy transfer from different sensitiser molecules (aromatic hydrocarbons, dyes, pigments, carbonyl compounds)[1,2,104,178] and participate in reactions involving the formation of hydroperoxides, the oxidation of C=C bonds, addition to diene systems, etc.[179–182] Tertiary amines, substituted phenols, chelate complexes, and β-carotene are used to suppress polymer photochemical oxidation processes.[179–182] Singlet oxygen is then quenched in exciplexes and in the case of β-carotene this is accompanied also by the *cis—trans* isomerisation reaction.

Thus many systems in which there is a possibility of the formation of intermolecular or intramolecular exciplexes, which initiate conversion processes, exhibit effective photostabilising properties.

4. Compounds containing a metal atom

As mentioned in Section II, a molecular system with a heavy atom usually has a short lifetime of the T state and can therefore be an effective photostabiliser. An example of systems of this type is provided by organometallic compounds (for example, ferrocenes) and metal chelates.[1,2] These compounds can be both UV radiation absorbers and quenching agents for excited states of the polymer or impurity molecules. We shall consider this question briefly.

Apparently the first experimental indication of the possibility of energy transfer from the polymer to the molecules of phenylferrocene and *o*-hydroxybenzoylferrocene, used to photostabilise melamine-alkyd coatings, was obtained by Schmitt and Hirt.[184] Ferrocene derivatives also protect other polymers against the action of light.[1]

Chelate complexes of heavy metal ions (Ni, Cr, Eu, etc.) with thiobisphenols quench the triplet state of the carbonyl group[185] and other chromophores.[1] For this reason alone, they exhibit photostabilising properties. However, it is known that not all metal chelates are quenching agents for the excited states of carbonyl groups.[2] Thus nickel thiophenoxide does not quench the T states of ketones but nevertheless exhibits photostabilising properties, which have been attributed to the involvement of this chelate in processes leading to the quenching of singlet oxygen molecules.[186,187] In terms of the efficiency of the quenching of singlet oxygen, metal chelates can be arranged in the following sequence depending on the nature of the metal: $Mn^{2+} \simeq Cu^{2+} < Co^{2+} < Ni^{2+} \simeq Fe^{3+}$. As already mentioned above, singlet oxygen may be quenched by the formation of complexes. In the case of metal chelates, the spin–orbit interaction, which is determined by the charge on the metal nucleus, is important for this quenching mechanism. This problem has not yet been considered theoretically.

If the quenching of excited states in polymers is associated with energy transfer to the photostabiliser molecule, it is subject to the same rules as in other molecular systems:[14] energy transfer takes place only when the energy at the lowest excited state of the acceptor is lower than the energy of the donor; triplet–triplet transfer occurs via an exchange-resonance mechanism while singlet–singlet transfer involves an inductive-resonance mechanism; the efficiency of the transfer increases with increase in the overlap integral for the emission spectrum of the donor and the absorption spectrum of the acceptor. When the photophysical properties of the photostabilising molecule are known, this permits conclusions about the mechanism of its action and a description of the dependence of the transfer constants on the type of photostabiliser molecule and the type of polymer.[188,189]

It is essential to note that the photostabilising effect of metal chelates does not reduce to the physical mechanism of their action, because they function also as activators of the non-radical decomposition of hydroperoxides and their efficiency depends also on the type of ligand.[190–192] Detailed studies have been made on the mechanism of the action and efficiency of the complexes most widely used to stabilise polydienes.[193] Similar results were also obtained in another investigation.[194]

New metal chelate stabilisers for butadiene rubber, polystyrene, and polyolefins have been proposed in recent years.[195–198] As a rule, their action does not reduce to a single mechanism but involves shielding processes, the quenching of excited states, and chemical inhibition of photoreactions.

VI. Synergistic mixtures of photostabilisers

Under the real conditions of industrial processing and use of articles made of polymer materials, the polymer is acted upon by different ageing factors (heat, light, oxidants, mechanical stresses, etc.), and different ones can predominate. In order to impart to polymer articles an increased useful lifetime, in practice one usually employs not individual stabilisers but their mixtures, which frequently exhibit a synergistic effect. Such synergistic mixtures can comprise UV absorbers and quenching agents, antioxidants (including PZA) and UV absorbers, quenching agents, and antioxidants of various types, etc. Ternary mixtures of stabilisers are sometimes used.

Thus a mixture of the 2-hydroxy-4-octyloxybenzophenone photostabiliser and PZA (Tinuvin 770) in proportions of 9:1 imparts a significantly greater photostability to polypropylene than when each stabiliser is used separately.[199] It has been shown[200] that the employment of PZA in a mixture with physical mechanism stabilisers makes it possible to increase the photostability of polypropylene and high- and low-pressure polyethylenes by a factor of 6–8. It has been reported that sheeting for agricultural purposes with a useful lifetime of 3–4 years has been developed in Hungary using mixtures of this type. A synergistic effect has been observed[201,202] when a mixture of Tinuvin 770 with the Tsissorb [Cis-sorb?] 531 photostabiliser (2-hydroxybenzophenone) was used.

The causes of the synergism between PZA and photostabilisers have been investigated.[203–205] It was shown for the first time in these studies that the synergistic effect depends on the cross-section of the polymer article: a significant effect is observed in articles with a cross-section greater than 1 mm. A diffusion mechanism of the synergistic effect has been put forward to account for this finding. The diffusion of photostabiliser molecules to the PZA from the bulk of the polymer and from its surface ensures the protection of the surface layer undergoing further chemical oxidation (the "depot" effect).

Similar ideas have been put forward in another study,[206] where the photostabilisation of polypropylene, polystyrene, high pressure polyethylene, and ABC resins was investigated using synergistic mixtures of PZA and UV absorbers. According to these ideas, in the case of thin-profile articles the synergistic effect is either small or is altogether absent. Apparently this was observed in a study[207] where mixtures of Tinuvin 770 with the Tsissorb 531 photostabiliser, Tinuvin 327, and the UV-1084, Negopex B, and Irgastab 2002 nickel chelates failed to give a synergistic effect when films up to 200 μm thick were used.

Interesting results for the stabilisation of polyurethane systems have been obtained.[208] The authors investigated the protection of these systems against photooxidative ageing using PZA, photostabilisers, and phenolic antioxidants as well as their mixtures. It was established that in the case of polymers containing aromatic fragments the use of synergistic mixtures of these three types of stabilisers is the most effective.

The most complete survey and theoretical consideration of numerous experimental data on the synergism between various types of stabilisers and auxiliary substances were carried out by Ivanov and Shlyapintokh.[209] They considered the nature of the synergistic effect in the photostabilisation of polymers and they assumed that the effect is based on the following mechanisms: (1) diffusional transfer of the antioxidant to the photoreaction zone generated by the UV absorber; (2) protection of the photostabiliser by the antioxidant; (3) the action of the main stabiliser during use and of

the additional stabiliser during the processing of the polymer; (4) the increase in the efficiency of the UV absorber in the presence of an antioxidant as a consequence of the change in the mechanism of chain termination; (5) protection of the polymer by auxiliary additives during the activation of the main stabiliser in the initial stage of the ageing process; (6) the effect of one stabiliser as a radical acceptor and of another as a compound decomposing hydroperoxides; (7) quenching of the excited states of the antioxidant by the photostabiliser; (8) the use of special additives to improve the distribution of stabilisers in the polymer; (9) the formation of effective stabilisers on reaction of stabilising additives; (10) regeneration of the effective stabiliser. The authors estimated the maximum synergistic effects based on these mechanisms and the optimum component ratios. They analysed the probable changes in the effects as the thickness of the polymer specimens, the light intensity, and temperature were varied. Mechanisms 1–5 and 7–9 were studied experimentally.

Synergistic mixtures containing photostabilisers have been proposed recently for the stabilisation of polyethylene,[210,211] automobile enamels,[212] enamels for polyurethane coatings,[213] and other polymer systems.[214–218]

It is important to emphasise that all the photostabilisers used in synergistic mixtures are systems in which the T states are either not populated or have a short lifetime.

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Thus analysis of theoretical and experimental data makes it possible to formulate requirements, in addition to those already well known, which must be satisfied by the photophysical properties of molecular systems with a high photostabilising efficiency. The possibilities in the search for new types of photostabilisers have been by no means exhausted since only a small number of systems with a limited set of the simplest reversible adiabatic photoreactions, initiating non-radiative conversion processes, have been used hitherto. The ideas described determine to a large extent the pathways followed in such search.

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β-Aminophosphonates and β-aminophosphinates, synthesis, and properties

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ABSTRACT. **Methods of obtaining β-aminophosphonates and β-aminophosphinates, their physical and chemical properties and also the practical application of these substances are reviewed.**

The bibliography contains 98 references.

Contents

I.	Introduction	807
II.	Methods of preparation	807
III.	Properties	813
IV.	Applications	815

I. Introduction

β-Aminoethylphosphonic acid (AEP) was isolated for the first time in 1959 from a living organism (molluscs) by Horiguchi and Kondatsu[1] who named it ciliatine. Other authors later isolated AEP and derivatives of it from other natural sources.[2–4] AEP is a component of cell membranes and protects them from degradation of cellular structure. There is currently a hypothesis that AEP is a vitamin or equates to one.[5] It has been established that AEP and its derivatives possess high biological activity.[6,7]

The chemistry of aminophosphonates and aminophosphinates has been discussed in several reviews but these are mainly devoted to α-aminomethylphosphonates[6–10] or the biochemistry of these substances.[11,12]

Preparative methods, chemical and physical properties, and the practical use of β-aminophosphonates and β-aminophosphinates are considered in the present review.

II. Methods of preparation

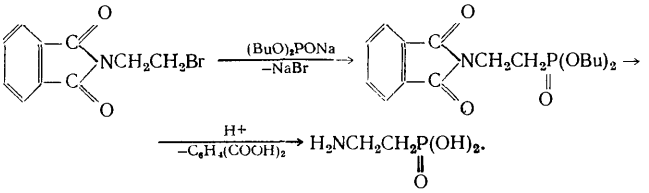
1. The Michaelis–Becker reaction

The method consists of the reaction of β-substituted ethyl halides with the sodium or potassium salt of a dialkyl phosphorous acid (Michaelis–Becker reagent).[13–22] The reaction is carried out in acid or other inert solvent.

AEP was synthesised for the first time by the Michaelis–Becker reaction in 1946.[13] On reacting the Michaelis–Becker reagent with the ethyl ester of β-bromopropionic acid a phosphonocarboxylic acid triester is formed. It was converted into the amide then AEP was obtained by a Hofmann rearrangement.

$$BrCH_2CH_2COOEt \xrightarrow[-NaBr]{(EtO)_2PONa} (EtO)_2P(O)CH_2CH_2COOEt \xrightarrow{NH_3} (EtO)_2P(O)CH_2CH_2CONH_2 \xrightarrow[2)\ H^+]{1)\ NaOBr} (HO)_2P(O)CH_2CH_2NH_2.$$

Soon afterwards AEP was synthesised by the reaction of sodium dibutyl phosphite with bromoethylphthalimide and subsequent hydrolysis with hydrobromic acid.[14]



When using β-bromoethylamine hydrobromide in place of the phthalimide the yield of AEP fell sharply probably as a result of the poor solubility of the initial hydrobromide in inert solvent.[15]

The Michaelis–Becker method is useful for introducing a phosphono group into a molecule of a compound in which there is a chlorine atom in the β position to an amino group.[16–19]

M I Kabachnik and collaborators[16] synthesised the dibutyl ester of a β-piperidino substituted phosphonate. This same compound was formed on oxidation of β-piperidinoethylphosphinic acid diester with manganese dioxide.

$$C_5H_{10}NCH_2CH_2Cl \xrightarrow{(BuO)_2PONa} C_5H_{10}NCH_2CH_2P(O)(OBu)_2 \xleftarrow{MnO_2} C_5H_{10}NCH_2CH_2P(OBu)_2$$

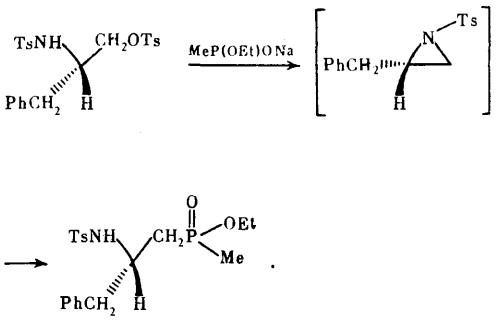
N-Alkyl- and *N*-silylaminophosphonates were obtained by the reaction of the corresponding *N*-substituted β-chloroethylamines with a Michaelis–Becker reagent.[17,19]

$$R'R''NCH_2CH_2Cl \xrightarrow{(EtO)_2PONa} R'R''NCH_2CH_2P(O)(OEt)_2.$$

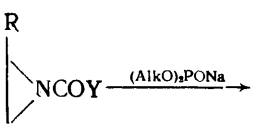
Maier has synthesised 'tris-AEP'.[18]

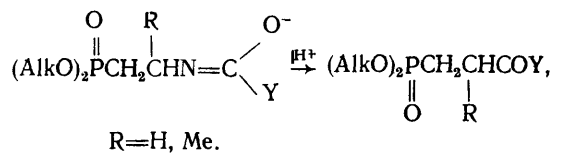
$$N(CH_2CH_2Cl)_3 \xrightarrow{(EtO)_2POK} N[CH_2CH_2P(O)(OEt)_2]_3 \xrightarrow{H^+} N[CH_2CH_2P(O)(OH)_2]_3.$$

A method[21] has been developed for obtaining optically active *N*-substituted β-aminoethylphosphonic acid and -phosphinic acids. An ester is formed by reacting an *N*-tosylaminotosylate with an excess of Michaelis–Becker reagent in tetrahydrofuran solution at room temperature and is converted into the acid by hydrolysis with 48% HBr.

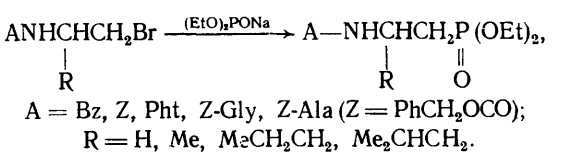


The reaction proceeds through an *N*-tosylaziridine intermediate. Aminophosphonates were obtained with high diastereoselectivity in relation to the chiral centre at phosphorus. *N*-Acyl substituted diesters of aminophosphonic acid were synthesised from *N*-acyl- or *N*-sulphonylaziridines and a Michaelis–Becker reagent.[22]





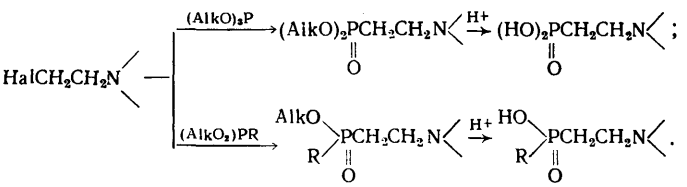
The Michaelis–Becker reaction is used for obtaining phosphonate analogues of aminoacids and peptides.[23]



Phthaloylglycine, benzoylglycine, carbobenzoxydipeptides, carbobenzoxyaminoacids, etc. were used as starting materials. The method has great importance since it affords the preparation of various phosphonic analogues of biologically active aminoacids containing functional groups and asymmetric centres and also of polyphosphonopeptides.[23]

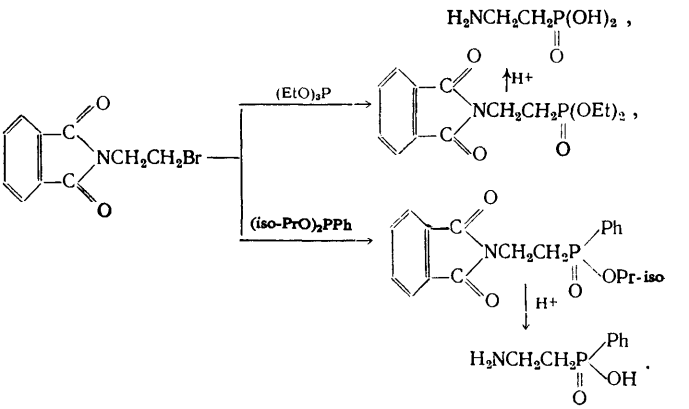
2. The Arbuzov reaction

The method comprises the introduction of an alkylphosphonic group with the aid of a trialkyl phosphite or dialkylaryl phosphonite into a molecule of *N*-substituted amine with the formation of a phosphorus–carbon bond and subsequent hydrolysis of the ester groups.[24–29]

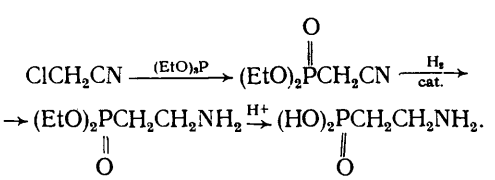


β-Aminoethylphosphonic acid was obtained by the Arbuzov reaction by heating β-bromoethylphthalimide with triethyl phosphite at 160 °C and subsequent hydrolysis of the ester groups.[25]

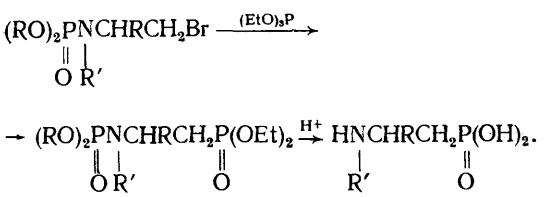
The reaction with *O,O*-diisopropyl phenylphosphonite proceeds in a similar manner, whereby β-aminoethylphenylphosphinic acid is obtained in good yield.[26]



An aminophosphonate is formed by reacting chloroacetonitrile with triethyl phosphite and subsequent reduction of the nitrile group. This compound is converted into AEP by hydrolysis of the ester group.[11]

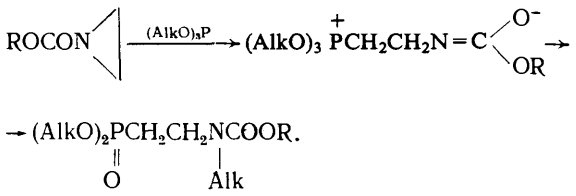


N-Substituted aminophosphonates containing substituents at the α- and β-carbon atoms have been obtained by the Arbuzov reaction.[27,28] *N*-Phosphorylated diesters are formed by reacting the β-bromoethylamide of a dialkyl phosphate with triethyl phosphite at 150–160 °C. Subsequent hydrolysis with hydrochloric acid leads to fission of the ester groups and the nitrogen–phosphorus bond forming β-aminoethylphosphonic acids.



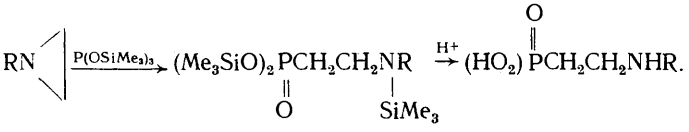
A non-classical variant of the Arbuzov reaction has been used to obtain *N*-acylated aminophosphonates.[24] *N*-Acylaziridines in place of alkyl halides were reacted with esters of trivalent phosphorus

acids. It was suggested that the reaction proceeds through a zwitterionic intermediate.



The hydrobromide of aminoethylphosphonic acid was isolated after further hydrolysis with hydrobromic acid.

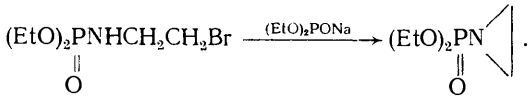
N-Acylaziridines react with *tris*-(trimethylsilyl) phosphite in a similar manner.[30]



Drawbacks of the method of obtaining aminophosphonates by the Arbuzov reaction are the time taken for the process and the forcing conditions of carrying out the reaction.

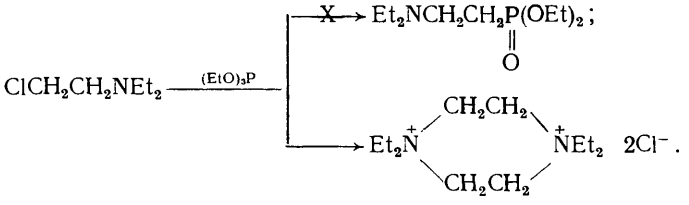
It should be mentioned that in certain cases it is possible to obtain an aminophosphonate (-phosphinate) only by the Arbuzov or Michaelis–Becker reactions.

An *N*-phosphorylated aziridine is formed by interacting the β-bromoethylamide of a diethyl phosphate with a Michaelis–Becker reagent.[28]



In this case the Arbuzov reaction is used to obtain the β-aminophosphonate.

The dimer of the initial amine is obtained on reacting β-chloroethyldiethylamine with triethyl phosphite.[17]



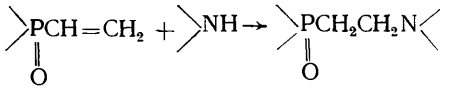
The reaction with *tris*-(β-chloroethyl)amine proceeds in a similar manner.[18]

The Michaelis–Becker and Arbuzov reactions do not have broad scope and are strictly specific methods for obtaining particular aminophosphonates and -phosphinates.

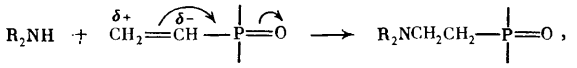
3. Addition to an unsaturated system

a) Addition of amines to a multiple carbon–carbon bond in phosphonates

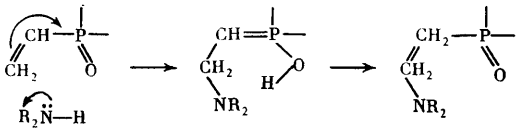
Addition of amines at a multiple carbon–carbon bond in phosphonates has been studied in fair detail.[16,31–48] In all cases addition occurs according to the inverse Markovnikov rule, i.e. the amino group is added to the β-carbon atom of the vinyl group.[32]



Kabachnik and collaborators[16,32] have interpreted the addition to the β-position by a shift of electrons under the influence of the electron-accepting group:



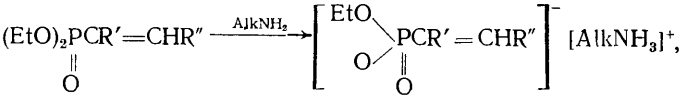
or by the formation of a transition complex.



The addition of amines to a diethyl vinylphosphonate has been studied.[35,36] The reaction proceeds most readily with secondary amines and with more difficulty with primary amines and ammonia.[35,36,38] Dimethylamine adds to diethyl vinylphosphonate without a catalyst at 20 °C.[13] Piperidine reacts similarly.[16,32,35] The reaction of vinylphosphonates with secondary amines usually proceeds with an equimolar ratio of reactants without a solvent or with a 10–15% excess of amine or in aqueous solution.[31,35,39]

Primary amines react only in the presence of a catalyst, such as an alkali metal alkoxide, in an excess of amine on heating.[19,35,38,40]

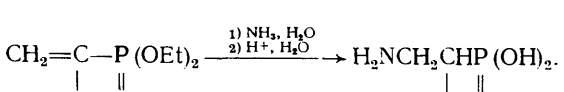
It should be mentioned that the action of alkylamines on a vinylphosphonate containing substituents at the α- or β-carbon atom leads to dealkylation of the initial phosphonate and the formation of an alkylammonium salt of the ethyl vinylphosphonate.[19]



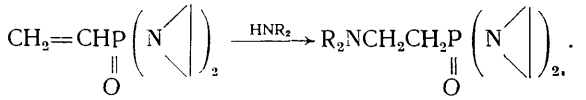
R′, R″ = Me, Ph.

The more basic aliphatic amines react more readily and give aminophosphonates in high yield. Diethyl vinylphosphonate reacts with butylamine in the presence of catalytic amounts of sodium ethoxide at 80–90 °C.[19,40] Diethyl vinylphosphonate reacts with aniline on heating on a water bath. The yield of diethyl *N*-phenylaminophosphonate was low due to the formation of a larger quantity of byproducts.[35,36] Sterically hindered amines [Me_3CNH_2, $(Me_3Si)_2NH$] did not add to vinylphosphonate in the presence of catalytic amounts of sodium ethoxide even on extended boiling (15–20 h) because of the spatial obstacles.[19]

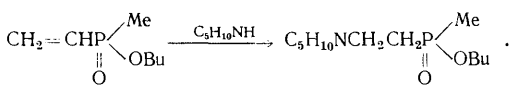
An aminoethylphosphonate with a free amino group was obtained in high yield by reacting a vinylphosphonate with ammonia in alcoholic solution in the presence of catalytic amounts of sodium methoxide.[35,36] α-Bromovinylphosphonate reacts with a concentrated aqueous solution of ammonia on heating for 10 min at 50–60 °C and subsequent hydrolysis of the ester groups with hydrochloric acid.[41,42]



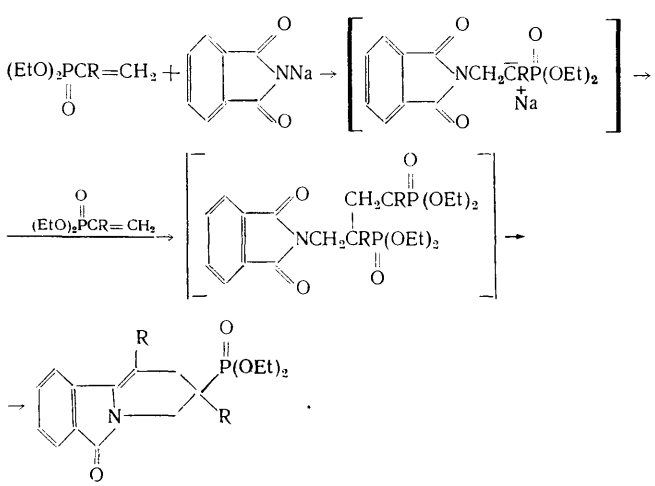
The rate of addition depends not only on the nature of the amine but also on the nature of the substituent at the phosphorus atom. An increase in electron-donating properties for the substituent at phosphorus significantly reduces the reaction rate.[43] This is caused by the different polarity of the multiple bond in imides and esters of vinylphosphonic acid. Vinylphosphonic acid diamides react with ethylenimine, diethylamine, piperidine and morpholine at 20 °C for 1.5–2 d or at 40–50 °C for 4–5 h. Allylamine and dibenzylamine add in the presence of catalytic amounts of sodium ethoxide.



Reaction of the butyl ester of methylvinylphosphonic acid with piperidine continued for 4 days at 20 °C and led to an almost quantitative yield of *N*-substituted phosphonate.[32]



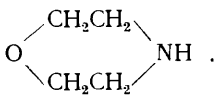
α-Substituted vinylphosphonates are synthons for preparing AEP and its derivatives.[49]



Various heterocyclic compounds were obtained by this method by treating vinylphosphonates with such imides as maleimide, succinimide and glutarimide.[49]

Reactions of vinylenediphosphonic acid with primary and secondary aliphatic and cyclic amines have been investigated. These were carried out in water or other highly polar media (H_2O–EtOH, AcOH) at 100–120 °C.[44–46]

$CH_2{=}C(PO_3H_2)_2 \xrightarrow{R'R''NH} R'R''NCH_2CH(PO_3H_2)_2$,
$R'R''NH$ = $MeNH_2$, $EtNH_2$, $(HOCH_2)_3CNH_2$, $HOCH_2CH_2NH_2$, $C_5H_{11}NH_2$, $C_7H_{15}NH_2$, $C_9H_{19}NH_2$, Et_2NH, $(HOCH_2CH_2)_2NH$, $(CH_2)_5NH$,



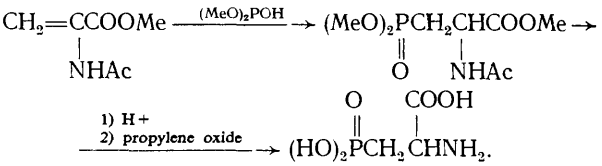
Usually a 2–6 fold molar excess of amine was used especially in the case of primary amines to suppress further reaction of products with the initial acid.

Investigation by TLC of the dependence of reaction rate on the pH of the medium showed the existence of an optimum region of pH values which was 7–9 for ethylamine, diethylamine and piperidine. At lower and higher pH values the reaction rate was sharply reduced. It was assumed that the optimum pH value must be lower than the pK_a of the nucleophile.[44–46] As was to be expected the sterically hindered *tris*-hydroxymethylaminomethane proved to be the least active. In difference to the indicated amines morpholine added at a high rate to the acid in the pH range 2–8.

b) Addition of dialkyl phosphites to unsaturated nitrogen-containing compounds

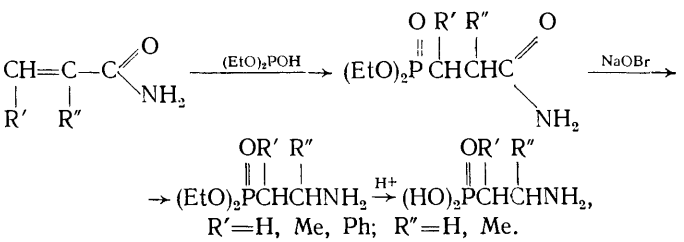
The addition of dialkyl phosphites to unsaturated compounds containing a carboxyl or carbonyl group has been described. The products were converted into amino compounds (by Hofmann, Curtius or Beckmann reactions).[11,50–52]

The ability of dimethyl phosphite to add to an activated carbon–carbon double bond has been demonstrated.[50] The phosphonic analogue of aspartic acid, where the β-carboxyl group is replaced by a phosphonate group, was obtained by the interaction of the methyl ester of *N*-acyl-α-aminoacrylic acid with dimethyl phosphite and subsequent hydrolysis.



Soroka and collaborators[53] improved this method by using esters of methyl- or ethylphosphonic acids in place of dimethyl phosphite. As a result the corresponding phosphinic analogues of aspartic acid were formed.

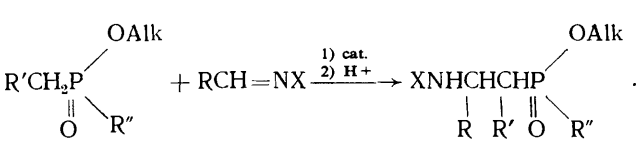
Carbamoyl phosphonates were formed on reacting amides of unsaturated acids with diethyl phosphite in the presence of catalytic amounts of EtONa. AEP or its analogues were obtained after several conversions and hydrolysis.[51,52]



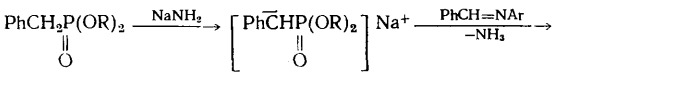
This reaction enabled AEP analogues to be obtained with various substituents on the α- and β-carbon atoms.[51]

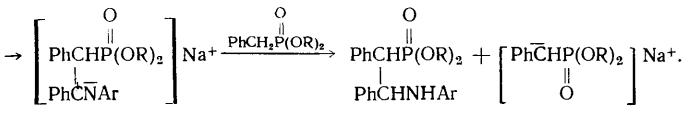
c) Addition of phosphonates at multiple carbon–nitrogen bonds

Aminophosphonates were obtained from Schiff's bases and phosphonates with an active methylene group in the presence of acidic or basic catalysts.[54–59]

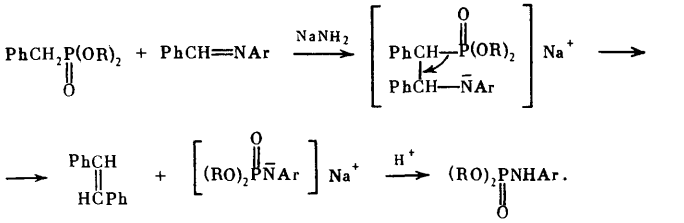


The reactions were investigated in the presence or absence of catalysts ($AlCl_3$, $NaNH_2$, $LiNH_2$) in ether and liquid ammonia at various temperatures. The influence was studied of the position of the substituent in the phenyl nucleus located on the nitrogen atom of the Schiff's base on the rate and route of the reaction. Optimum conditions were established for forming aminophosphonates. The following reaction mechanism was proposed.





The reaction did not proceed without a catalyst. In the presence of an excess of catalyst breakdown of the intermediate probably occurs and olefins are formed.

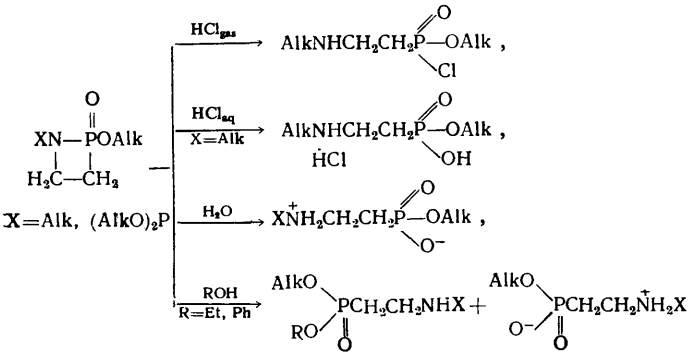


Chlorine in the *meta*-position of a benzene ring on the nitrogen atom increases the yield of aminophosphonate by 5–10%. The influence of electron-donating substituents varies depending on the position in the benzene ring. A methyl substituent in the *ortho*-position increases the yield of aminophosphonate, in the *para*- and *meta*-positions it aids dephosphorylation and the formation of olefins. The aminophosphonate is formed in 52–88% yield on reacting equimolar quantities of phosphonate and azomethine in the presence of catalytic amounts of sodium amide at 10–15 °C in ether.[54]

This method is very important since it affords the possibility of obtaining 1,2-substituted *N*-aryl-, *N*-carboxyl- and *N*-acylamino-phosphonates which are difficult to obtain by other routes.

4. Decomposition of 1,2-azaphosphetidines

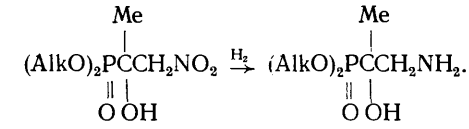
Monoesters of *N*-substituted aminoethylphosphonates are readily formed in almost quantitative yield by the action of hydrogen chloride, water or hydrochloric acid on 1,2-azaphosphetidines.[60–63] Diesters of aminophosphonates, together with the monoester, are formed on reaction with alcohol or phenol. Yields of mono- and diesters were not high because of the formation of reaction byproducts.



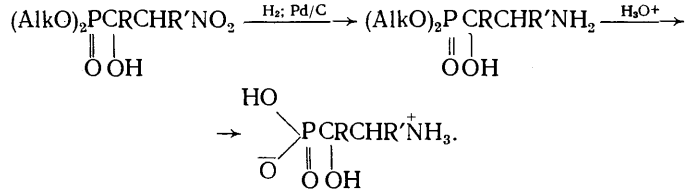
5. Reductive amination

a) Reduction of nitro compounds

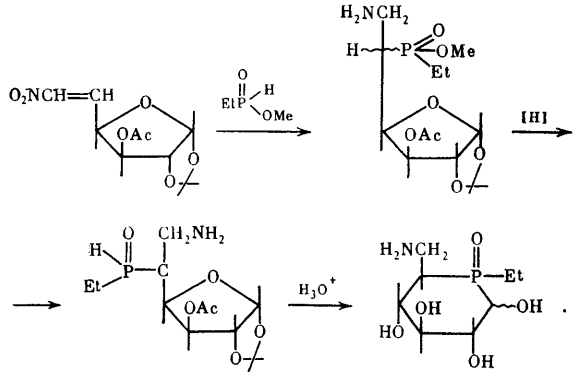
Aminophosphonates have been obtained by the reduction of nitro groups in phosphonates in the presence of Raney nickel catalyst.[64–67]



The hydrogenation of α-hydroxy-β-nitroalkylphosphonates over a neutral 5% palladium on carbon catalyst proved to be more successful. Aminophosphonates were obtained in high yield. They gave AEP analogues on hydrolysis with hydrochloric acid (1 : 1).[64–66,68,69]

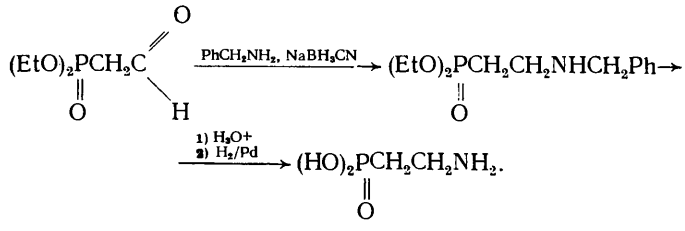


Japanese authors[70] have carried out hydrophosphorylation of a carbohydrate nitrovinyl derivative with the methyl ester of ethylphosphonic acid then reduction of the nitro and phosphono groups in the adduct obtained with the aim of taking off protecting groups. An original cyclisation reaction occurred.

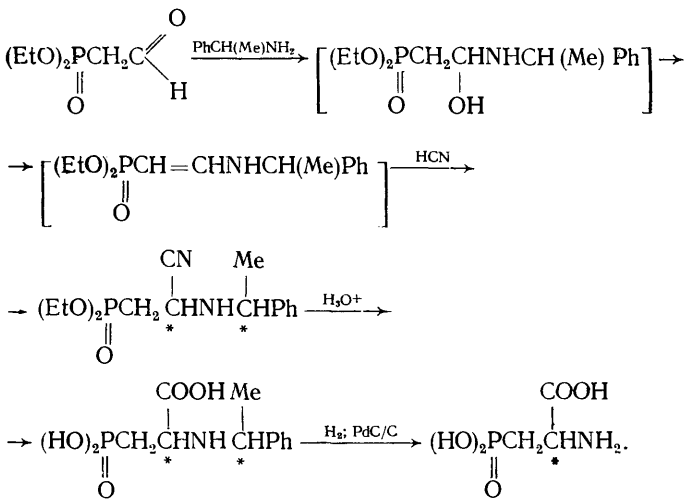


b) Reduction of azomethines

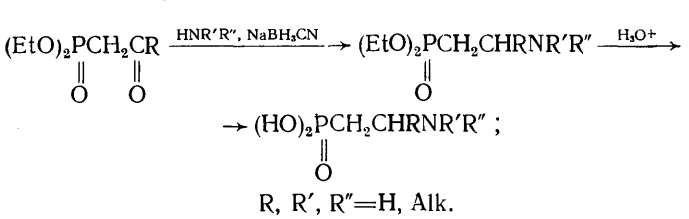
N-Benzylaminophosphonates are formed on condensing phosphonaldehydes with benzylamine in the presence of sodium cyanoborohydride.[71] Hydrogenolysis in the presence of palladium catalyst was used to remove the protecting *N*-benzyl and obtain a free amino group.



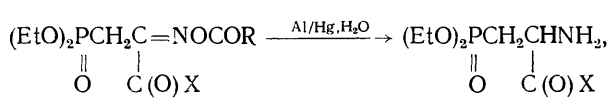
Phosphonaldehydes react with $S(-)$α-methylbenzylamine in the presence of HCN with the formation of optically active *N*-substituted aminophosphonates with an enantiomeric excess of 50%. Removal of the α-methylbenzylamino group by hydrogenolysis in the presence of a 10% palladium on carbon catalyst, followed by hydrolysis of the ester groups at the P atom with hydrochloric acid to obtain β-phosphonylalanine, occurred without epimerisation.[72]



Ketophosphonates,[73,74] like phosphonoaldehydes[71] also condense readily with amines in the presence of sodium cyanoborohydride. The reaction takes place in methanol at 20 °C and aminophosphonates are formed in high yield. β-Aminoethylphosphonic acids, either mono-*N*-substituted or containing a free amino group were obtained by hydrolysis of the ester groups at the P atom.[73]



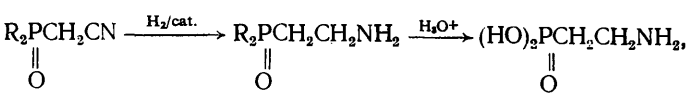
An interesting method of obtaining β-phosphonylalanine by reduction of *O*-acylated oximes with aluminium amalgam has been proposed.[75]



This method is convenient for the synthesis of various β-phosphorylated derivatives of α-aminopropionic acid.[75]

c) Reduction of the nitrile group

Aminoethylphosphonates are formed on reducing phosphonacetonitriles.[76–79]

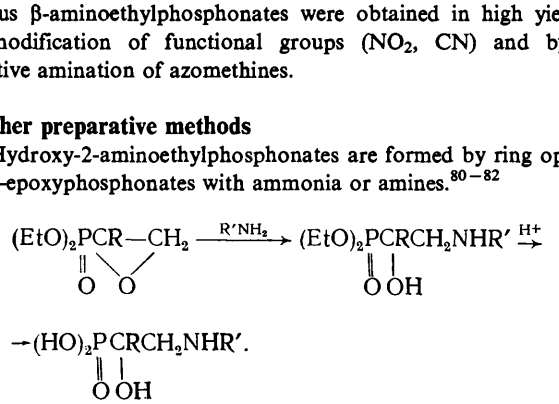


Hydrogenation was carried out in alcoholic ammonia solution in the presence of Rh/Al_2O_3 catalyst[76] and other additives preventing polymerisation at the increased pressure of 3–4 atm.[78] Dimethyl amido- and diethyl cyanomethylphosphonates were readily hydrogenated in the presence of Raney nickel catalyst and on hydrolysis gave AEP.[77–79] Palladium (10%) on carbon was also used as catalyst for the reduction of the CN group in diethyl cyanomethylphosphonate.[79]

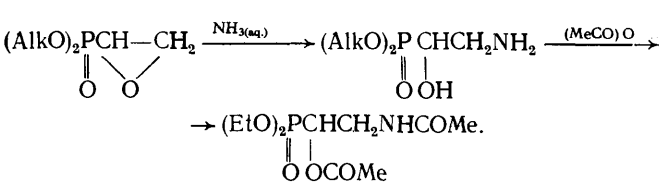
Thus β-aminoethylphosphonates were obtained in high yield by the modification of functional groups (NO_2, CN) and by the reductive amination of azomethines.

6. Other preparative methods

1-Hydroxy-2-aminoethylphosphonates are formed by ring opening of 1,2-epoxyphosphonates with ammonia or amines.[80–82]



The interaction of dialkyl 1,2-epoxyethylphosphonates with ammonia and with aniline has been investigated.[81] It was established that the reaction proceeded more readily with ammonia. With an excess of aqueous ammonia at 20 °C a distillable substance was obtained which was identified by conversion into the acetyl derivative.

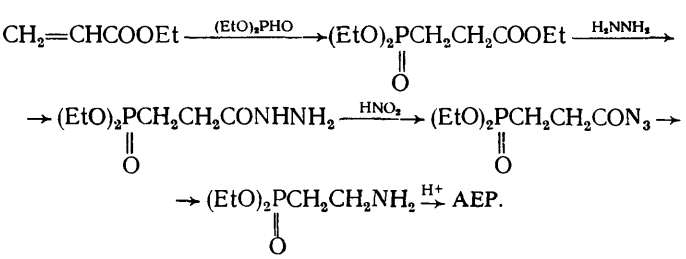


With aniline reaction occurred at 120–125 °C and took 24 h.

A method has been patented for obtaining *N*-substituted aminodiphosphonates by the action of ammonia, arylamines and dialkylamines on 2,2-diphosphonyloxirane.[82]



A method has been proposed for obtaining AEP by a scheme comprising addition of diethyl phosphite to an unsaturated compound, several transformations and subsequent hydrolysis of the resulting diethyl β-aminoethylphosphonate.[11]



Aminophosphonates are formed in high yield on reacting diethyl β-bromoethylphosphonate with diethylamine or dibutylamine.

The reaction was effected by boiling with an excess of amine in aqueous solution.[83]

$$(EtO)_2PCH_2CH_2Br \xrightarrow[H_2O]{Et_2NH} (EtO)_2PCH_2CH_2NEt_2.$$

Reaction with aziridine was carried out in a similar manner in aqueous solution in the presence of triethylamine.[84]

$$(EtO)_2PCH_2CH_2Br \xrightarrow[Et_3N]{HN} (EtO)_2PCH_2CH_2N$$

Synthesis of a carbamate of β-aminophosphonic acid has been effected starting from the diester of β-phosphonocarboxylic acid. This was converted into the azide which was then subjected to a Curtius rearrangement to give the carbamate.[85]

$$(EtO)_2PCH_2CH_2COOH \xrightarrow[PhCH_2OH,\ Et_3N]{(PhO)_2PON_3} \rightarrow (EtO)_2PCH_2CH_2NHC(O)OCH_2Ph.$$

This reaction has been used to obtain *N*-substituted urethanes and ureas.[86]

$$(AlkO)_2PCH_2CH_2NCO \xrightarrow{Alk'OH} (AlkO)_2PCH_2CH_2NHCOOAlk',$$
$$(AlkO)_2PCH_2CH_2NCO \xrightarrow{ArNH_2} (AlkO)_2PCH_2CH_2NHCONHAr.$$

This phosphonic and phosphinic analogues of aspartic acid have been obtained using the Strecker reaction.[87,88]

$$R(EtO)P(O)CH_2CHO \xrightarrow[2)\ H_3O^+]{1)\ NaCN,\ RNH_2\cdot HCl} R(HO)P(O)CH_2CHNHR\cdot COOH.$$

β-Aminoethylphenylphosphinic acid was formed on oxidation of a phosphine with hydrogen peroxide.[89]

$$PhP(H)CH_2CH_2NH_2 \xrightarrow{2H_2O_2} PhP(O)(OH)CH_2CH_2NH_2.$$

Diesters of 2-benzylimidazolylmethylphosphonic acid were synthesised by reacting *C*-phosphorylated imidates with *o*-phenylenediamine.[90]

$$(RO)_2PCH_2C(=NH\cdot HCl)OR' \xrightarrow[-R'OH,\ -NH_4Cl]{-NH_2,\ -NH_2} \text{benzimidazole-}CH_2P(O)(OR)_2.$$

A method has been suggested for obtaining optically active β-aminophosphonates and -phosphinates.[21,91]

III. Properties

1. Physical properties

β-Aminoethylphosphonic and -phosphinic acids are colourless, high melting, crystalline substances, soluble in water, less well in ethanol, nitromethanol and other polar solvents. The potentiometric titration curve for the amino acids has three discontinuities corresponding to the three ionisation constants of these compounds.[12] As for other aminophosphonic acids, they have a zwitterionic structure.[8] Polymorphism is a characteristic of AEP, two crystalline forms of it are known, an α form of rhombic plates and a β of needles, which is more stable.[11,12,79] The melting point is near 280 °C, however depending on the form the melting point may vary up to 20 °C.[12]

The diesters of *N*-alkylaminoethylphosphonic acids are colourless liquids, distillable in vacuum. The diesters of 1-hydroxy-2-aminoethyl phosphonic acids are thick viscous liquids, decomposing on distillation in vacuum.

There are broad absorption bands in the infra-red spectra of 1-hydroxy-2-aminoethylphosphonic acids in the 2700–3400 cm^{-1} region characteristic of the zwitterionic $PO^-\ldots NH_3^+$ with strong hydrogen bonds.[66] The zwitterionic structure is also confirmed by the presence of bands at 1620–1660 and 1520 cm^{-1} characteristic of NH and NH_3^+ deformation vibrations. The absorption frequency of the phosphoryl group is lowered to 1120–1150 cm^{-1}. An absorption band in the region of 3260 cm^{-1} is characteristic of OH group vibrations.

A significant low frequency shift was observed in the IR spectra of the mono ester of aminophosphonic acid[61] for the stretching vibrations of the N–H group in the 2750–2400 cm^{-1} region in comparison with the IR spectrum of the diester [ν(NH) 3280 cm^{-1}], where it was overlapped by the bands of C–H stretching vibrations,[61] which is characteristic for quaternary ammonium bases. The splitting of P=O group stretching vibrations in the 1230–1190 cm^{-1} region indicates the formation of associates.

A specific absorption for the amino group of AEP esters was detected in the 3500–3300 cm^{-1} region.[75]

The ^1H and ^{31}P NMR spectra have been studied in detail.[19,21–24,28,41,49,61,62,67,71–75,77,80,81,85,87,88,91,92]

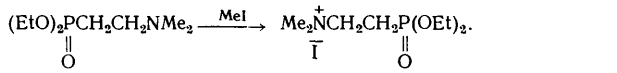
2. Chemical properties

a) Interaction with electrophilic reagents

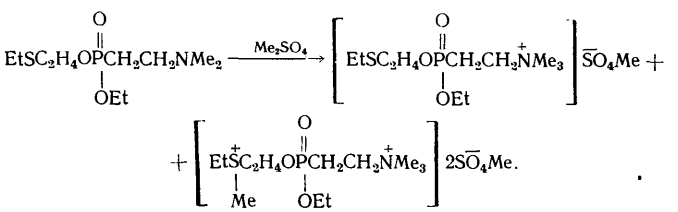
The diesters of *N*-monosubstituted aminophosphonates display the properties of proton-containing nucleophiles. They are readily phosphorylated by dialkyl chlorophosphites in the presence of triethylamine, are alkylated by alkyl halides, and add to isocyanates and *N*-oxides.[19,28,61,75]

$$(EtO)_2PCH_2CH_2NHR \xrightarrow[Et_3N]{(AlkO)_2PCl} (AlkO)_2PN(R)CH_2CH_2P(O)(OEt)_2,$$
$$(EtO)_2PCH_2CH_2NHR \xrightarrow[Et_3N]{(AlkO)_2POCl} (AlkO)_2PN(R)CH_2CH_2P(O)(OEt)_2,$$
$$(EtO)_2PCH_2CH_2NHR \xrightarrow[R=H,\ Alk]{R'NCO} R'NHCON(R)CH_2CH_2P(O)(OEt)_2,$$
$$(EtO)_2PCH_2CH_2NHR \xrightarrow{ArC\equiv N\rightarrow O} ArCN(R)CH_2CH_2P(O)(OEt)_2,$$
$$(EtO)_2PCH_2CH_2NHR \xrightarrow[R=P(O)(OAlk)_2]{AlkHal} RN(Alk)CH_2CH_2P(O)(OEt)_2.$$

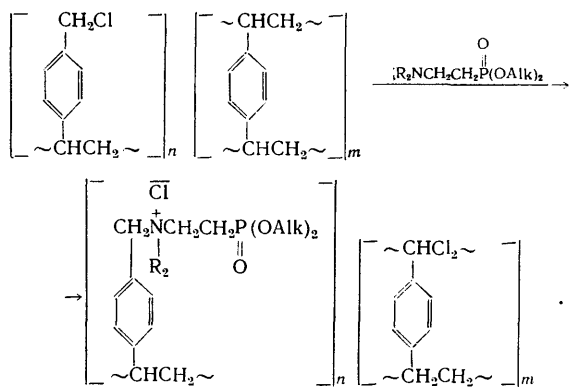
N-Disubstituted aminophosphonates are also readily alkylated by methyl iodide or dimethyl sulphate with the formation of salts, viz. the iodides or methosulphates of the corresponding aminophosphonates.[31,33,93]



On reacting *O*-ethyl-*O*-(β-ethylmercaptoethyl)-β-dimethylaminophosphonate with dimethyl sulphate the *N*-methyl methosulphate and *N*,*S*-dimethyl dimethosulphate were formed in the ratio 1 : 2.[33]



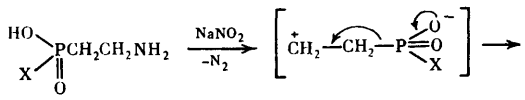
N-Disubstituted aminophosphonates react with the chloromethylated copolymer of styrene with divinylbenzene in a similar manner.[94] The reaction is usually carried out in a medium of the aminophosphonate at 90 °C in a nitrogen atmosphere.



b) Diazotisation

The diazotisation of aminophosphonates and -phosphinates has been studied.[26,69,95] It was established that the reaction proceeded through a carbocation intermediate and, depending on the structure, may go by two routes: rearrangement with migration of the phosphono group to a carbon atom with reduced electron density[95] or decomposition (fragmentation) with the formation of unsaturated compounds and inorganic phosphate.[26,69]

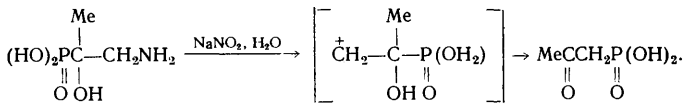
Diazotisation of aminophosphonates and -phosphinates containing an OH-group on the phosphorus atom is usually accompanied by fragmentation with the formation of olefins (in 70–80% yield), inorganic phosphate, vinylphosphonic acids and other contaminants.[26] The reaction was carried out with sodium nitrite in aqueous solution at 100 °C.



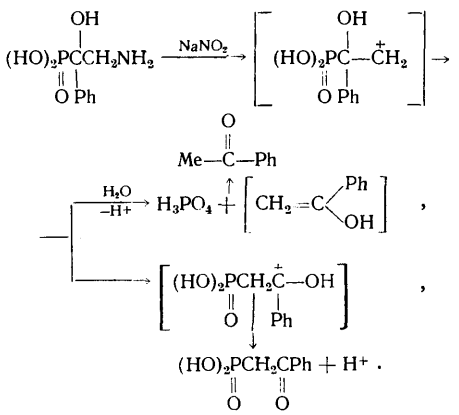
→ $CH_2=CH_2$ + inorganic phosphate,

X = OH, Ph.

When two substituents (methyl and OH-group) are present on the α-carbon atom a rearrangement occurs with migration of the phosphonic fragment and formation of 2-ketopropanephosphonic acid.[80]

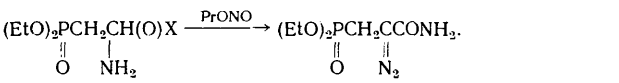


If the substituents on the α-carbon atom are OH and Ph then mainly (80%) rearrangement and only insignificant (7%) fragmentation occurs.[69]



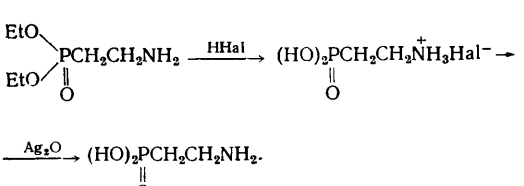
The reaction takes place at room temperature.

A diazo compound is formed on diazotising aminophosphonate with propyl nitrite in the presence of catalytic amounts of acetic acid.[75]

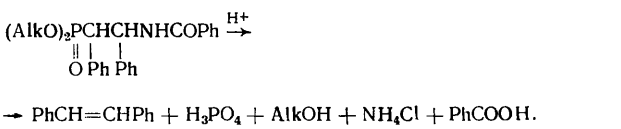


c) Hydrolysis

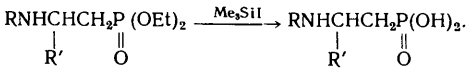
Conversion of esters of β-aminoethylphosphonic acids into the free acids is usually effected by hydrolysis in acid medium. Hal^- is removed using silver oxide,[26] propylene oxide, butylene oxide,[23,40,50] sodium hydroxide,[61] or aniline[66,68] or an aqueous solution of the aminophosphonate hydrochloride is passed through a column of Dowex 50W-X2 (H-form) ion exchange resin.[41,53,75]



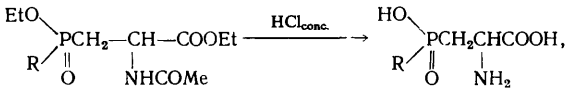
Exceptions are diesters of 1,2-diphenyl-substituted aminophosphonates which are decomposed on boiling in 20% HCl with the formation of olefin.[58]



Esters of aminophosphonic acids are converted into acids by the action of trimethylsilyl iodide[23] or trimethylsilyl bromide.[92]



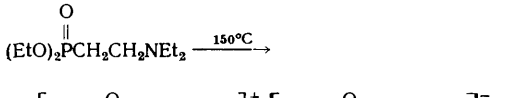
An *N*-acetyl group on an aminophosphonate may be converted into a free amino group by boiling with an excess of HCl for 10–12 h.[53]

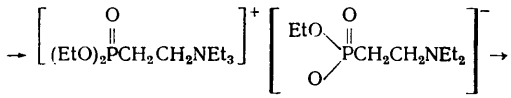


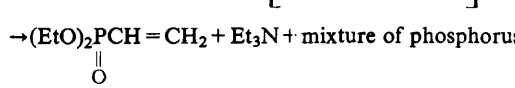
R = Me, Et, EtO.

d) Stability

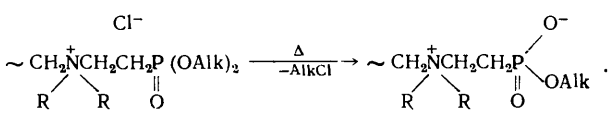
Diesters of 1-hydroxy-2-aminoethylphosphonic acid have low stability,[66,68] are decomposed on distillation[81] and were isolated as picrates which are then used for their purification and identification.[66,68] In contrast the diesters of β-aminoethylphosphonic acid are stable under normal conditions. On heating at 150 °C for 34 h they are decomposed with the formation of diethyl vinylphosphonate, triethylamine and a mixture of oxyacids of phosphorus.[17] It was proposed that an intermolecular reaction occurred with the formation of an intermediate salt which decomposed and gave diethyl vinylphosphonate. The presence of triethylamine was explained by an intramolecular alkylation.





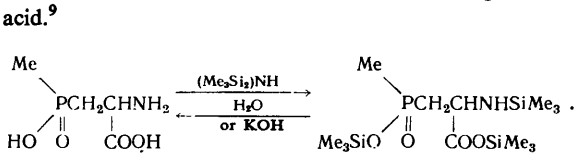


On heating the diester of an *N*-polymer-containing β-aminoethylphosphonic acid at 130 °C an intramolecular ionic rearrangement occurs with the formation of the monoester.[94]



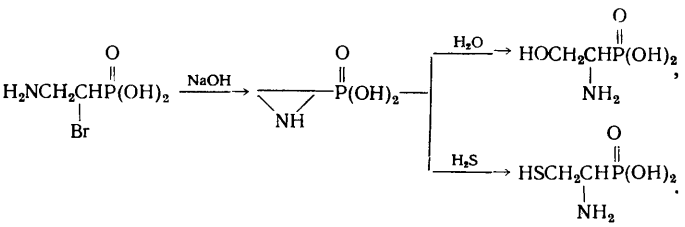
e) Other reactions

On reacting an aminoethylmethylphosphinic acid with an excess of hexamethyldisilazane an *N*-silylated derivative is formed which on treatment with water or alcohol is converted once again into the initial acid.[9]



This method has been proposed for purifying such compounds.[9]

α-Bromo-β-aminoethylphosphonic acid is cyclised in an alkaline medium to aziridinephosphonic acid.[41,42] Fission of the aziridine ring by the action of water or hydrogen sulphide leads to the formation of the phosphonic analogues of serine and cysteine respectively.



It is possible in this way to go from β-aminophosphonic to α-aminophosphonic acids.

IV. Applications

Diesters of aminophosphonic acid possess bactericidal, fungicidal and also antipyretic action.[76,96]

β-Amino-substituted phosphonates and -phosphinates display high extraction properties.[6,7,48,91,94,98] Their important advantage is the combination of good selectivity with high extractive ability.

N-Substituted phosphonic acids have been proposed as extractants and for imparting fire-resistant properties to cellulose material.[82] They possess complexing ability, immunotropic activity and may find application as chelating complexants for multicharged ions, flotation agents, and pharmaceutical preparations.[44,46]

β-Phosphonylalanine displays antiblastic action.[88] The introduction of a CH_3 group in place of an OH at phosphorus sharply reduces the cytostatic activity.[88]

The synthesis of medicinal preparations based on β-aminophosphonic acids is promising.[5,23]

The material presented shows the promise of these compounds. It is possible to be confidant that these compounds will find wide application not only in laboratory practice, but also in medicine, agriculture and other branches of the national economy.

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Progress in the chemistry of sulphilimines

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ABSTRACT. The information obtained during recent years on the structure, methods of synthesis, and properties of sulphilimines has been correlated.

The bibliography includes 155 references.

Contents

I. Introduction 819
II. Nature of the S(IV)=N bond and structure of sulphilimines 819
III. Methods for the synthesis of sulphilimines 820
IV. Reactions of sulphilimines 824

I. Introduction

The chemistry of sulphilimines or ~~sulphimides~~[1] originated in 1917 after the discovery[2] of the oxidative imination of sulphides, which resulted in a solution to the problem of contamination by mustard gas. Starting from this period the chemistry of sulphilimines has evolved quite rapidly and at the present time is a relatively well-developed branch of organoelemental chemistry.

Convenient preparative methods for obtaining sulphilimines have been developed, their properties have been studied thoroughly, and areas of their practical application have been found.

The interest shown in the chemistry of sulphilimines by many research workers is mainly due to the synthetic importance of these compounds. The lability of the S(IV)=N bond, its ability to be cleaved by both nucleophilic and electrophilic reagents, and also the two active reaction sites (sulphur and nitrogen) provide sulphilimines with the properties of valuable reagents for organic synthesis.

On the other hand, some examples of this class of compounds have the properties of antioxidants of polyolefins[3] and herbicidal, bactericidal, and pharmacological reagents, which also stimulates a particular interest. The chemistry of sulphilimines up to 1976 is covered by several review articles,[1,4,5] one of which[1] is exhaustive. However, since the time of publication of these articles a considerable amount of new information that requires correlating has accumulated, and this has provided the contents of the present review.

II. Nature of the S(V)=N bond and structure of sulphilimines

There is no common view about the nature of the S(IV)=N bond in sulphilimines and in other imino compounds of sulphur, although much attention has been given to this question in the literature.[6–22] This is because the S(IV)=N bond is different from a normal double bond since for elements of the third and subsequent periods of the Periodic Table of chemical elements the overlap of *p*-atomic orbitals (*p*-AOs) is energetically unfavourable. At the same time the structural features positively indicate the multiple nature of this bond but with a low π-order and with a length greater than the corresponding sum of the covalent radii and a high polarity and low potential barrier of internal rotation which does not allow diastereomeric compounds to occur as a result of hindered rotation about the S(IV)=N bond. The lability of the S(IV)=N bond varies over a wide range according to the nature of the substituents on the sulphur and nitrogen atoms. An analysis of these factors and also an analysis of information about the nature of the E=N bond of other organoelemental compounds provided a basis for the assumption that the *d* orbitals of the sulphur atom participate in the formation of the S(IV)=N bond in sulphilimines. This assumption incorporates three basic theories developed during recent years about the nature of the S(IV)=N bond in sulphilimines.

1. The S(IV)=N bond is a normal double bond in which a second bond is formed as a result of overlap between the *p* orbitals of the nitrogen atoms and *d* orbitals of the sulphur atom that have the corresponding symmetry.

2. The S(IV)=N bond is a semipolar bond in which a σ-bond is formed from AOs of *p* type from the sulphur and nitrogen atoms and the second bond is ionic, stabilised through the formation of a charge transfer complex from the electron-rich nitrogen atom (=NR groups) to the sulphur atom with a positively charged R_2S skeleton.

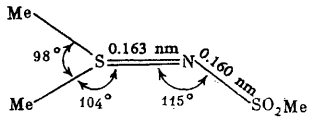
3. The S(IV)=N bond is a double bond in which the π-bond is stabilised through the interaction of the p_π (or *n*) orbitals of the nitrogen atom with the d_π orbitals of the sulphur atom or by a hyperconjugation effect which occurs as a result of the interaction between the unshared electron pair of nitrogen with the electrons of the antibonding σ orbitals of the neighbouring S–C bond ($n_N-\sigma_S^*$ interaction).

A detailed analysis of these three theories about the nature of the S(IV)=N bond, including quantum-mechanical calculations, structural and spectroscopic data, did not lead Egorov[21] to any definite conclusion about the nature of the S(IV)=N bond in sulphilimines. It was stated[21] that sulphilimine molecules $R_2S=NY$ and compounds isoelectronic to them are characterised by a mobile π-electron system, including as an important factor 3*d* orbitals, the population of which increases with an increase in the effective electronegativity of the substituents on the S atom and decreases in the presence of π-electron-acceptor groups on the nitrogen atom. The stabilisation energy of the S(IV)=N bond through $d_\pi-p_\pi$ conjugation is generally small and varies according to the same sequence of change in properties of substituents R and Y. Stabilisation is achieved to a greater extent through the electrostatic interaction between sites with opposite charges—the $R_2\overset{+}{S}$ and $N\overline{Y}$ groups.

On this basis Egorov[21] has proposed that the electronic structure of the S=N bond can be represented as three main resonance structures:

$$S{=}\ddot{N}{-}Y \leftrightarrow \overset{+}{S}{-}\overset{-}{\ddot{N}}{-}Y \leftrightarrow \overset{+}{S}{-}\ddot{N}{-}\overline{Y}.$$

The crystalline and molecular structures of *S*, *S*-dimethyl-*N*-methanesulphenylsulphilimine and certain *N*-arenesulphonylsulphilimines, derived using X-ray diffraction analysis, have been reported in the literature.[6,7,13,15,21] A characteristic feature of these structures is that the tetracovalent sulphur atom together with its surrounding valence bonds forms a trigonal pyramid which is quite stable towards pyramidal inversion, and this is also confirmed by the fact that sulphilimines with suitable substituents can exist in enantiomeric forms caused by the chirality of the sulphur atom. Characteristic bond lengths and bond angles are given below for a typical example of a sulphilimine—*S*,*S*-dimethyl-*N*-methansulphonylsulphilimine



The two C–S(IV) bonds in the molecule of this sulphilimine have different lengths (0.180 nm and 0.178 nm) in the crystalline state, while in solution or the liquid state these bonds are almost equal, which is due to the relatively low rotational barrier of the S(IV)=N bond, the magnitude of which can be assessed from the results of calculations on the hypothetical molecule of $H_2S{=}NH$ (9.60 kcal mol^{-1}).[23] The average length of the S(IV)–C bond is less than the sum of the respective covalent radii (0.183 nm), which is attributed to the possible hyperconjugative type of interaction between the Me groups and the sulphur atom. The bond lengths and bond angles in the molecules of other sulphilimines have very similar values (Table 1). A comparison of the physical parameters of the E=N bond (E = S, Se, Te) of sulphilimines, selenimines,[23] and tellurimines[24] revealed an increase in the length of this bond on going from sulphur to tellurium, which is consistent with the increase in covalent radii of the respective elements.

The frequencies of the stretching vibrations of the S(IV)=N bond (symmetrical and antisymmetrical), according to the literature data,[4,17–19,21] occur over a broad spectroscopic region from 750 to 1400 cm^{-1}, which leads to the assumption that the π-system of the S(IV)=N bond is highly polarisable. It is natural that the high polarisability of the bond is responsible for the considerable dependence of the position of the absorption bands on the nature of the groups on the sulphur and nitrogen atoms, having also a considerable effect on the polarity of the S(IV)=N bond, which varies over a wide range from 1.56 to 10.1 D.[25]

III. Methods for the synthesis of sulphilimines

All methods known at the present time for the synthesis of sulphilimines are based on the use of sulphides and sulphoxides and other tetracovalent sulphur compounds as the initial reactants.

1. Synthesis of sulphilimines from sulphides

a) Oxidative imination of sulphides with *N*-halo compounds

The reactions which are accompanied by the oxidation of an element and formation of an imino group are usually known as oxidative imination.[26] The oxidative imination of sulphides was first discovered by Raper,[2] who showed that mustard gas (β,β′-dichlorodiethyl sulphide) reacts with sodium *N*-chloro-*p*-toluenesulphonamide to form a physiologically inactive compound. It was reported by Nicolet and Willard[27] in 1921 that the product of the reaction between diethyl disulphide and sodium *N*-chloro-*p*-toluenesulphonamide was a colourless crystalline compound. Nicolet and Willard[27] were not able to establish the structure of this compound, and it was only in 1922 that Mann et al.[28] showed that the reaction between disulphides and sodium *N*-chlorosulphonamides results in the formation of sulphilimines.

$$R{-}S{-}R + ArSO_2NNaCl \rightarrow RRS{=}NSO_2Ar + NaCl,$$

R = Et, $ClCH_2CH_2$; Ar-*p*-MeC_6H_4.

However, not all sulphides are capable of reacting with sodium *N*-chlorosulphonamides to form sulphilimines. It was reported as early as 1922 by Mann and Pope[28,29] that an increase in the number of chlorine atoms in the alkyl groups of the sulphides reduces the capacity of the latter to undergo imination with sodium *N*-chlorosulphonamides. Leandri and Spinelli[30] showed for the reaction between sodium *N*-chloro-*p*-toluenesulphonamide with the bis-sulphides RS–X–Sr (X = Ph, –CH=CH–, $-CH_2-$, $-CH_2-CH_2-$, and others) that both terminal and internal electron-acceptor groups inhibit the process of imination and the *p*-toluenesulphonylimino group introduced as a result of imination of the first sulphur atom inhibits imination of the second sulphur atom. Therefore bis-sulphilimines were only obtained in the case of bis-sulphides in which the sulphur atoms were separated by three or more methylene groups.

Table 1. S(IV)=N bond lengths and angles in sulphilimines $RR^1S{=}NR^2$.

R	R^1	R^2	S=N bond lengths, nm	Bond angles, deg		Refs.
				C–S^{IV}–N	C–S^{IV}–C	
Me	Me	2-$NO_2C_6H_4$	0.1622	106.5 (100.9)*	99.5	[15]
$(-CH_2-)_3$	—	4-$NO_2C_6H_4$	0.1649	—	—	[20]
Me	Me	4-$NO_2C_6H_4$	0.1651	—	—	[20]
Me	Me	$MeSO_2$	0.1627	104.1	98.2	[13]
Me	Me	4-$MeC_6H_4SO_2$	0.1636	102.2	98.4	[13]
Ph	Ph	4-$CH_3C_6H_4SO_2$	0.1628	103.8	101	[21]
Me	Me	PhCO	0.1659	104.2 (99.5)	101	[6]
Me	Me	CCl_2CO	0.1667	104.7 (98.5)	99.9	[22]
Et	Et	$CHCl_2CO$	0.1633	103.8 (99.2)	99.3	[21]

*The second C–S(IV)–N angle is given in brackets.

The effect of the groups on the sulphur atom on the ability of sulphides to undergo imination with sodium *N*-chlorosulphonamides was studied in greater detail by Kucsman et al.[31–34] They established that in the case of the reaction between sulphides and

sodium *N*-chlorosulphonamides in aqueous media that the corresponding sulphoxides are formed together with *N*-arenesulphonylsulphilimines

$$R_2S + ArSO_2NNaCl \xrightarrow{H_2O} \begin{cases} \rightarrow R_2S=NSO_2Ar + NaCl \\ \rightarrow R_2S=O + ArSO_2NH_2 + NaCl \end{cases}$$

In this case the ratio of sulphilimines to sulphoxides depends on the nature of the groups on the sulphur atoms in the initial sulphide, the pH of the reaction medium, and the type of solvent used. In the opinion of Kucsman et al.,[31,32] the ability of sulphides to undergo imination with sodium *N*-chlorosulphonamides is determined by the degree of electron density on the sulphur atom, which should be sufficiently high for the sulphur atom to be able to displace the chloride anion on the nitrogen atom of the *N*-chloroamide, in other words, Kucsman et al. considered that imination of sulphides occurred by nucleophilic substitution and that the formation of sulphoxides was due to the hydrolysis of sulphilimines. They subsequently concluded[35,36] that the imination of sulphides with sodium *N*-chlorosulphonamides was more complex. In their opinion, the sodium *N*-chlorosulphonamide undergoes conversion in an aqueous alcoholic medium as a result of an equilibrium reaction to *N*-chlorosulphonamide (rapidly) and to *N,N*-dichlorosulphonamide (slowly), which are quite reactive electrophilic reagents

$$2ArSO_2NNaCl \overset{H_2O}{\rightleftarrows} 2ArSO_2NHCl + NaOH,$$

$$ArSO_2NHCl \rightleftarrows ArSO_2\bar{N}Cl + H^+,$$

$$ArSO_2NHCl + ArSO_2\bar{N}Cl \rightarrow ArSO_2NCl_2 + ArSO_2\bar{N}H.$$

The formation of *N*-chlorosulphonamides and *N,N*-dichlorosulphonamides was also reported in other studies,[37–39] and the participation of *N,N*-dichlorosulphonamides in this process is supported by their use as iminating agents on reacting with sulphides,[40–43] which, however, is frequently accompanied by other side reactions.

On reacting with *N*-chlorosulphonamides or *N,N*-dichlorosulphonamides, sulphides form a chlorosulphonium cation $R_2\overset{+}{S}Cl$, which reacts with a sulphonamide anion $ArSO_2\bar{N}X$ (X = H, Cl) to form a sulphilimine, while hydrolysis of the chlorosulphonium cation gives a sulphoxide[35,44,45]

$$R_2S + ArSO_2NClX \rightarrow R_2\overset{+}{S}Cl + ArSO_2\bar{N}X,$$

$$R_2\overset{+}{S}Cl \begin{cases} \xrightarrow{ArSO_2\bar{N}X} R_2S{=}NSO_2Ar + XCl \\ \xrightarrow{\bar{O}H} R_2S{=}O + HCl \end{cases}$$

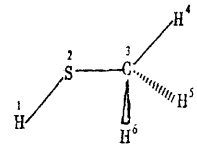
This interpretation of the mechanism for oxidative imination of sulphides with sodium *N*-chlorosulphonamides is consistent with the effect on this process of different factors, namely, the pH of the medium, the type of solvent used, and the nature of the groups on the sulphur atom in the initial sulphide. A low pH of the medium assists the conversion of sodium *N*-chlorosulphonamide to the more active *N*-chloro- and *N,N*-dichloro-sulphonamides but reduces the probability of the existence of the sulphonamide anion. According to the results of Tsujihara et al.[45] in the case of the imination of dialkyl and alkyl aryl sulphides with sodium *N*-chloro-*p*-toluenesulphonamide, a pH of 6 is the most favourable. As solutions of sodium *N*-chlorosulphonamides are alkaline, the addition of a small quantity of acetic acid to the reaction medium increases the yield of sulphilimines.[46–48] Because of the low solubility of sodium *N*-chlorosulphonamides in organic solvents, aqueous solutions of methanol, acetone, dioxan are used as the reaction medium for imination of sulphides as are two-phase media such as water–methylene dichloride, which naturally reduces the yield of sulphilimines and assists the formation of sulphoxides. Yamamoto et al.[49] showed that the use of anhydrous organic solvents such as methylene dichloride as the reaction medium and *N*-chloro-*N*-(dialkylamino)arylsulphonamides, which are readily soluble in these solvents, instead of sodium *N*-chlorosulphonamides, results in the sole formation of sulphilimines in quantitative yield

$$R_2S + R^1(R^2)NN(Cl)SO_2Ar \rightarrow R_2S{=}NSO_2Ar + R^1R^2NCl.$$

When two-phase reaction media are used, phase-transfer catalysts also help to increase the yield of sulphilimines.[50,51]

The susceptibility of the sulphur atom in a sulphide to electrophilic attack by a chlorine cation depends directly on the magnitude of its electron density, which is determined by the nature of the groups on the sulphur atom. Electron-acceptor groups on the sulphur atom in the sulphide hinder imination or make it impossible. Hence, the search for and development of methods for increasing the electron density on the sulphur atom in sulphides is important in terms of theory and synthesis. An analysis of the effective charges on the sulphur atom in the methanethiol molecule and its carbanion, obtained by quantum-mechanical calculations using the CNDO/2 method (Tables 2 and 3) shows[52] that one such method is to form an α-carbanion site in the sulphide molecule.

Table 2. Order of σ bond (*P*) and effective atomic charges (*q*) in the methanethiol molecule.[52]

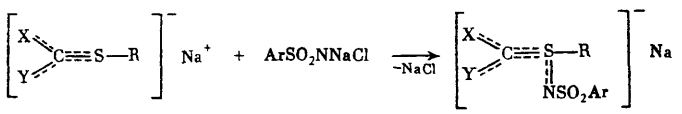


Atom No.	*q*	Bond	*P*
1	−0.011	1–2	0.685
2	−0.043	2–3	0.773
3	−0.059	3–4	0.664
4	0.043	3–5	0.665
5	0.035	3–6	0.665
6	0.035	—	—

A reduction in electron density on the sulphur atom from the effect of electron-acceptor groups in the molecule of the initial sulphide should be balanced in a carbanion by the displacement of charge from the carbanion site.

Koval' et al.[53] demonstrated the basic possibility that arylsulphonylimination of diacylmethyl aryl sulphides containing a mobile α-H atom together with electron-acceptor groups can occur, but the sulphilimines resulting in this case undergo further conversions as a result of imino–ylide tautomerism. The use of their sodium salts instead of these sulphides assists the

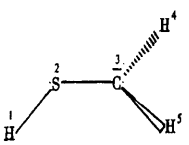
arylsulphonylimination of these compounds in anionic form, as well as the stabilisation of the anion of the resulting *N*-arylsulphonylsulphilimines.[52,54–56]



$R = 2\text{-}NO_2C_6H_4$, $4\text{-}NO_2C_6H_4$, $2,4\text{-}(NO_2)_2C_6H_3$; X = Y = PhCO, X = Y = MeCO, X = Y = CN, X = Y = EtOCO;

X = MeCO, Y = EtOCO.

Table 3. Order of σ bond (*P*) and effective atomic charges (*q*) in the methanethiol carbanion.[52]



Atom No.	*q*	Bond	*P*
1	−0.140	1–2	0.675
2	−0.346	2–3	0.827
3	−0.357	3–4	0.661
4	−0.079	3–5	0.661
5	−0.079	—	—

Other *N*-chloro compounds such as chloramines,[57] *N*-chlorocarboxamides,[58] *N*-chlorourethane,[59] *N*-chloroamidines,[60] *N*-chloroguanidines,[61] and *N*-chlorourea and its derivatives[62,63] react with dialkyl and alkyl aryl sulphides to form aminosulphonium salts, which are converted by bases to the corresponding sulphilimines.

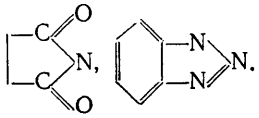
$$R_2S + XNHZ \rightarrow R_2\overset{+}{S}NHZX^- \xrightarrow[-HX]{HB} R_2S{=}NZ,$$

HB – base; X = Cl, Br; Z = H, Alk, Ar, Hetar, AlkCO,

ArCO, EtOCO, R—C(=NR)—, NH_2—N=CH—, NH_2CO.

Sources of chlorine cations are also provided by chlorine,[64] t-butyl hypochlorite,[65–69] sulphuryl chloride,[70] *N*-chlorosuccinimide,[64,71,72] and other heterocyclic *N*-chloro compounds,[64] which react with sulphides at low temperatures to form chlorosulphonium intermediates that are converted by *N*-nucleophiles to sulphilimines.

$$R_2S + Cl{-}Z \rightarrow [R_2\overset{+}{S}{-}Z]\overline{Cl} \xrightarrow{R'NH_2} R_2\overset{+}{S}NHR'\overline{Cl} \xrightarrow[-HCl]{HB} R_2S{=}NR',$$

Z = Cl, t-BuO, SO_2Cl, 

Aliphatic, aromatic, and heterocyclic amines, *N*-aminophthalimide, cyanamide, and sodium sulphonamides and carboxamides are used as *N*-nucleophiles.

b) Oxidative imination of sulphides with hydroxylamine derivatives

The oxidative imination of sulphides with hydroxylaminosulphuric acid, first described by Appel and Buchner,[73,74] is a specific case of the general imination of sulphides with hydroxylamine derivatives and particularly with *N*-arylsulphonyl-*O*-*p*-nitrophenylsulphonylhydroxylamine,[75] *N*-ethoxycarbonyl-*O*-*p*-nitrophenylsulphonylhydroxylamine,[75] and *O*-mesitylsulphonylhydroxylamine.[76,77]

$$R_2S + XNHOY \rightarrow R_2\overset{+}{S}NH(X)\overline{O}Y \xrightarrow[-YOH]{HB} R_2S{=}NX,$$

X = H, $ArSO_2$, EtOCO;

Y = HSO_3, $2,4,6\text{-}(Me)_3C_6H_2SO_2$, $4\text{-}NO_2C_6H_4SO_2$.

The mechanism of this reaction has not been studied, but it is possible from literature data[26] on the oxidative imination of tertiary phosphines with hydroxylaminosulphuric acid to suggest that there are two mechanisms, one involving the generation of an imene ṄH and the other, more probable, mechanism involving nucleophilic attack by sulphide on the electron-deficient nitrogen atom.

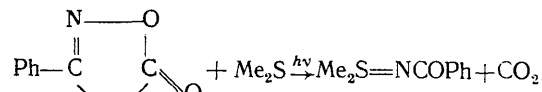
c) Reaction of sulphides with nitrenes

Sulphilimines are formed in good or moderate yield by reaction of sulphides with nitrene generated by photochemical, thermal, and chemical methods. A method involving the photolysis of different organic azides in the presence of an excess of disulphide is the most widely used.

$$XN_3 \xrightarrow{h\nu} NX: \xrightarrow{R_2S} R_2S{=}NX,$$

X = $ArSO_2$, PhCO, EtOCO, R_2PO and others.

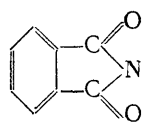
The reaction has been studied in a series of arenesulphonyl,[78] acyl,[79] alkoxycarbonyl,[79] diphenylphosphonyl and dialkylphosphonyl[80] azides. It has been proposed[81] that sulphides react more rapidly with singlet than with triplet nitrenes since the presence in the reaction mixture of products that give rise to the formation of triplet nitrenes inhibits the formation of sulphilimines. The low yields of sulphilimines may be due to their photochemical instability. At the same time during photolysis the sulphilimines themselves are sources of nitrenes, as has been noted[79] in the case of the photolysis of *S,S*-dimethyl-*N*-ethoxycarbonylsulphilimine. Sources of nitrenes are also provided by certain unstable heterocyclic compounds, photolysis of which in the presence of sulphides results in the formation of sulphilimines[82]



The main disadvantage of the method for synthesising sulphilimines by reaction between sulphides and thermally generated nitrenes is the thermal instability of the resulting sulphilimines, which has been observed in the case of the thermolysis of acyl azides,[83] alkoxycarbonyl azides,[83,84] and arylsulphonyl azides[83,85] in the presence of sulphides. It has been shown[86] that in the presence of copper the thermolysis of azides, and hence the reaction between nitrenes and sulphides, occurs at a lower temperature, which helps to increase the yield of sulphilimines.

Chemical generation of nitrenes in order to obtain sulphilimines has been used less often. In the literature there have been reports on only a few sulphilimines by reaction between sulphides and arenesulphonamides[87,88] and *N*-aminophthalimide[1] in the presence of lead tetraacetate

$$R_2S + NH_2X \xrightarrow{Pb(OAc)_4} R_2S{=}NX,$$

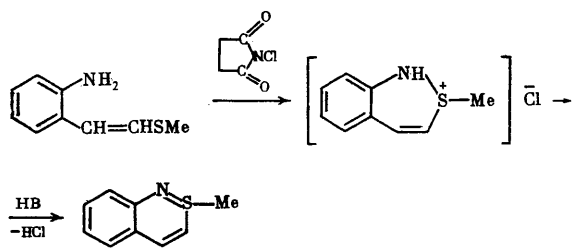
$X = ArSO_2$, 

It cannot be excluded that the formation of sulphilimines in the reaction between sulphides and compounds with an E=N bond (E = S, I), as reported in the literature,[89,90] also occurs via a stage involving generation of nitrenes

$$R_2S + X{=}NTs \rightarrow R_2S{=}NTs,$$
$$X = TsN{=}S,\ ArI$$

d) Oxidative cyclisation of aminosulphides

On treatment with *N*-chlorosuccinimide, aromatic amines containing alkylthio groups at the *ortho*-position form cyclic aminosulphonium salts, which in the presence of bases are converted to cyclic sulphilimines[91,92]



2. Synthesis of sulphilimines from sulphoxides

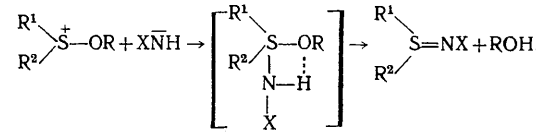
a) Condensation of sulphoxides with amides and amines in the presence of activating electrophilic reagents

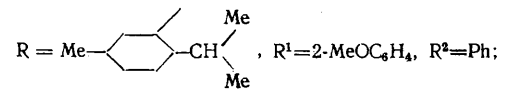
This method involves the generation of active sulphonium salts by the attack of an electrophile on the oxygen atom of a sulphoxide, which is converted to an effective leaving group

$$R_2S{=}O \xrightarrow{E^+} R_2\overset{+}{S}OE \xrightarrow[-HOE,\ -H^+]{R^1NH_2} R_2S{=}NR^1,$$
E – electrophile.

Phosphorus pentoxide,[93] trifluoroacetic anhydride,[93,94] sulphur trioxide, sulphuric acid, and boron trifluoride[95] have been used as activating electrophiles. Amides of sulphonic and carboxylic acids and certain amines have been used as *N*-nucleophiles. A number of sulphilimines have been obtained by the reaction of sodium sulphonamides and carboxamides with alkoxysulphonium salts.[68,96]

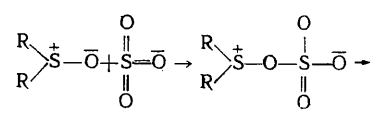
The reaction is stereospecific and occurs with retention of configuration at the sulphur atom, which in the opinion of research workers is due to the formation of an intermediate four-membered cyclic compound which is stabilised by an intramolecular hydrogen bond.

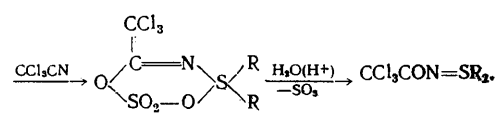




X=$ArSO_2$, CH_2ClCO, $CHCl_2CO$, CCl_3CO, CF_3CO.

The sulphonium salts formed by reaction of sulphoxides with sulphur trioxide react with nitriles to form sulphinylimines.[97] The proposed mechanism of this reaction involves attack by the electron-deficient carbon atom of the nitrile group on one of oxygen atoms of the sulphonium salt, which only takes place for nitriles containing strong electron-acceptor groups:



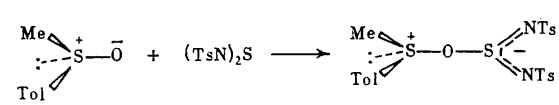


b) Condensation of sulphoxides with *N*-substituted amides

With certain *N*-substituted amides containing groups with polar double bonds as substituents, condensation of sulphoxides takes place in the absence of activating electrophilic reagents.[98–101]

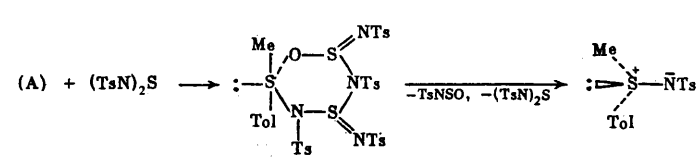
$$R_2S{=}O + YN{=}X \rightarrow R_2S{=}NY + XO,$$
$$X = SO,\ CO,\ S{=}NSO_2Ar,\ SCl_2;\ Y = ArSO_2,\ RCO,\ EtOCO,\ Ar.$$

The condensation mechanism has been studied in detail in the case of the reaction between methyl *p*-tolyl sulphoxide and *N,N'*-bis(*p*-toluenesulphonyl)sulphurdiimide.[102] It involves attack by the electron-deficient atom of the polar group on to the oxygen of the sulphoxide to form the sulphonium salt (A), whose subsequent conversion is determined by the nature of the solvent.

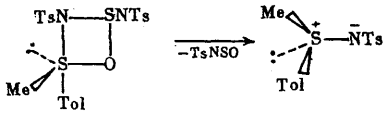


(A)

In pyridine, reaction of the sulphonium salt with a second molecule of sulphurdiimide results in the formation of a six-membered transition state, whose conversion to a sulphilimine is accompanied by inversion of configuration at the chiral sulphur atom.

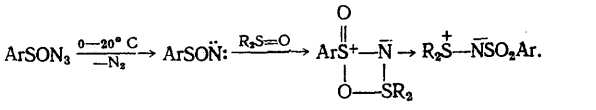


In benzene the reaction takes place via a four-membered transition state with retention of configuration at the sulphur atom.



c) Reaction of sulphoxides with arylsulphinyl azides

In contrast to arylsulphonyl azides, which form *N*-arylsulphonylsulphoximides with sulphoxides,[103] arylsulphinyl azides react with sulphoxides to form *N*-arylsulphonylsulphilimines.[104] It is thought that intermediate arylsulphinylnitrenes react with sulphoxides to form unstable four-membered cyclic compounds that are converted to a sulphilimine:



3. The use of other tetracovalent sulphur compounds in the synthesis of sulphilimines

a) Nucleophilic substitution on a tetracovalent sulphur atom

Nucleophilic substitution of different atoms and groups on a tetracovalent sulphur atom in order to obtain sulphilimines is utilised in two methods. The first of these involves nucleophilic substitution of halogen atoms[105,106] or alkoxy groups[105,107] in order to produce a S(IV)=N bond

$$R_2SX_2 + 3NH_3 \rightarrow R_2S{=}NH + 2NH_4X,$$

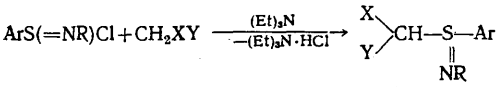
R = Ar, CF_3, X = Cl, F;

$$Ph_2S[OC(CF_3)_2Ph]_2 + RNH_2 \rightarrow Ph_2S{=}NR + 2PhC(CF_3)_2OH,$$

R = H, Alk, Ar, $ArSO_2$.

The second method involves nucleophilic substitution of halogen atoms on the tetracovalent sulphur atom in order to produce an S(IV)–C bond.[108,109]

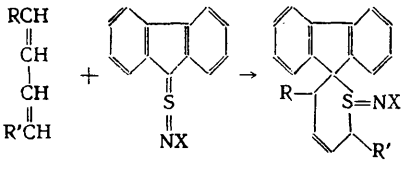
$$F_2SNPh + 2PhLi \rightarrow Ph_2S{=}NPh + 2LiF,$$



R = $(Me)_3C$, $(Me)_2C(CN)$, $ArSO_2$; X = CN, MeCO; Y = CN, MeCO, EtOCO.

b) Reaction between thione-*S*-imines and diene hydrocarbons

It has been shown[110] that *N*-substituted thione-*S*-imines containing arylsulphonyl groups as substituents can perform as active dienophiles in [4 + 2] cycloaddition reactions with conjugated diene hydrocarbons to form sulphilimines containing a sulphur atom in the ring.



R = H, Me; R′ = Me, H; X = *p*-$MeC_6H_4SO_2$.

IV. Reactions of sulphilimines

All of the reactions involving sulphilimines can be divided into three groups, according to the type of change to the S(IV)=N bond: a) reactions that take place without change to the S(IV)=N bond; b) reactions that take place with conversion of the S(IV)=N bond to an S(II)–N or S(IV)–N bond; c) reactions that take place with cleavage of the S(IV)=N bond.

1. Reactions of sulphilimines that take place without change to the S(IV)=N bond

a) Modification of substituents on the sulphur and nitrogen atoms

The directed chemical modification of different substituents on the sulphur and nitrogen atoms in sulphilimines is widely used in the synthesis of new types of these compounds. Particularly convenient in this respect are *S*-haloalkylsulphilimines, which as a result of nucleophilic substitution of the halogen atoms[111] or dehydrohalogenation[112] can readily be converted to new types of sulphilimines.

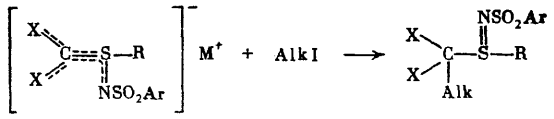
$$ArSO_2N{=}S(Me)CH_2X + RNa \xrightarrow[-NaX]{} ArSO_2N{=}S(Me)CH_2R,$$

X = Cl, Br; R = AlkO, ArO, PhS, NCS;

$$ArSO_2N{=}S(R)CH_2CH_2X \xrightarrow[-HX]{HB} ArSO_2N{=}S(R)CH{=}CH_2,$$

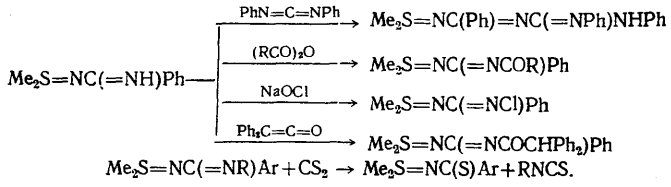
X = Cl, Br; R = Ph, 4-MeC_6H_4.

Replacement of the metal in metal salts of *N*-arylsulphonylsulphilimines by alkyl groups also gives new types of sulphilimines[52,55,56]



X = CN, MeCO, EtOCO; M = Na, Ag; R = 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$.

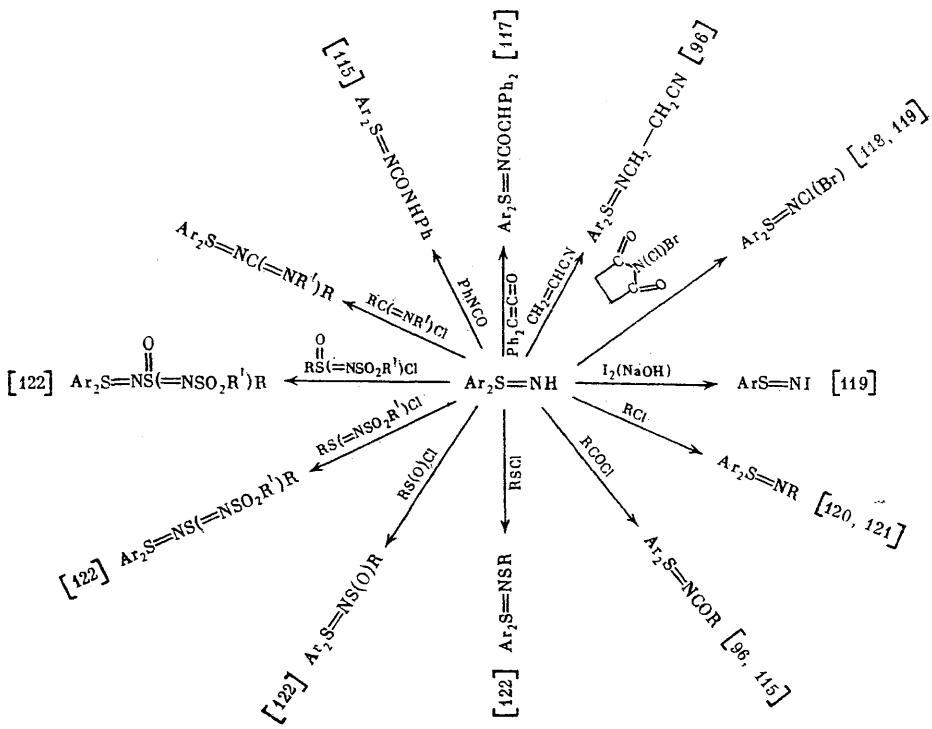
Examples of the modification of groups on the nitrogen atom of *N*-substituted sulphilimines are shown by the reactions of these groups with various reagents, as described in three studies[60,113,114]



$$Me_2S{=}NC(=NR)Ar + CS_2 \rightarrow Me_2S{=}NC(S)Ar + RNCS.$$

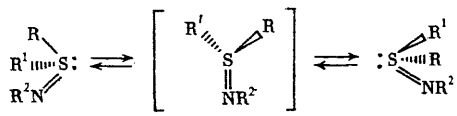
For the synthesis of new types of *N*-substituted sulphilimines, very frequent use is made of sulphilimines that are unsubstituted on the nitrogen atom and which are formed as a result of acid cleavage of

the S(IV)–N bond in *N*-arylsulphonylsulphilimines when they are reacted with 90% sulphuric acid.[115–119]



b) Thermal racemisation of sulphilimines

Sulphilimines with different substituents on the sulphur atom can exist in enantiomeric forms because of the chirality of the sulphur atom. When the temperature is increased interconversion of enantiomers occurs by a pyramidal inversion mechanism via a planar transition state.



Kinetic studies on the thermal racemisation of optically active sulphilimines 2-$MeOC_6H_4S(=NR)Ph$ (R = $PhSO_2$, 4-$MeC_6H_4SO_2$, 4-$MeOC_6H_4SO_2$, MeCO, PhCO, CF_3CO, etc.) which occurs at 75 °C in chloroform showed[123] that together with the known factors for affecting the rate of thermal racemisation (type of solvent, steric factors, etc.) an important part is played by the nature of the groups on the nitrogen atom. Strong electron-acceptor groups on the nitrogen atom reduce the rate of thermal racemisation.

Thus, for example, the rate of thermal racemisation of *N*-tosylsulphilimines is 15 times slower than the rate of thermal racemisation of *N*-trifluoroacetylsulphilimines. In the opinion of Moriyama et al.,[123] this occurs because strong electron-acceptor groups inhibit the $2p-3d$ changes in formation of the S(IV)=N bond in the transition state and also lower the repulsion between the free electron pairs, since they substantially reduce the electron density on the nitrogen atom in the pyramidal geometry of sulphilimines. Therefore, *N*-substituted sulphilimines that contain weak electron-acceptor groups as substituents adopt a configuration that is almost planar. The rate of pyramidal inversion decreases as the absorption frequency of the stretching vibrations due to the S(IV)=N bond decreases in the IR spectra, which is an indication that an increase in the bipolar nature of the S(IV)=N bond increases the barrier of pyramidal inversion.

c) Oxidation of sulphilimines

Sulphilimines are as a rule stable towards oxidation, and they are only oxidised in the presence of strong oxidising agents to form sulphoximides

$$R_2S{=}NR' \xrightarrow{\text{oxidation}} R_2S(=O){=}NR'.$$

R = Alk, Ar; R′ = H, Ar, $ArSO_2$, RCO, ROCO.

The oxidising agents most frequently used are potassium permanganate,[96] hydroperoxides of aromatic carboxylic acids,[115,122] ruthenium tetroxide,[124] hydrogen peroxide in an alkaline medium,[125] and sodium hypochlorite.[126,127] During oxidation in two-phase media, phase-transfer catalysts—Bu_4NX (X = Cl, Br, ClO_4, HSO_4), $PhCH_2N(Et)_3Cl$, $C_{12}H_{15}N(Me)_3Cl$, and others—have been used.[126,127]

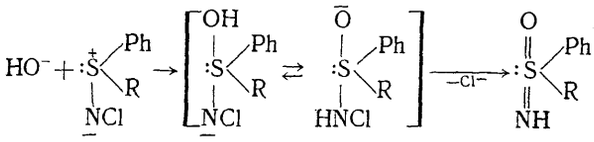
d) Alkaline hydrolysis of sulphilimines

Hydrolytic cleavage of sulphilimines in the presence of mineral acids has been known for a long time and is well studied. As a rule it leads to the corresponding sulphoxides and initial *N*-nucleophiles whatever the structure of the initial sulphilimine. Hydrolysis of sulphilimines in the presence of bases has been insufficiently studied up to now. The composition and structure of the products of this

hydrolysis are frequently determined by different factors and primarily by the structure of the initial sulphilimine. It was reported,[128] for example, that the alkaline hydrolysis of 1-(*N*-*p*-toluenesulphonyl)tetrahydrothiophenesulphilimine in an alcoholic medium results in the formation of 2-alkoxytetrahydrothiophene and *p*-toluenesulphonamide. Alkaline hydrolysis of *N*-chlorosulphilimines in an aqueous medium results in the formation of sulphoximides with an unsubstituted nitrogen atom.[118]

$$R_2S{=}NCl \xrightarrow[-HCl]{H_2O(OH^-)} R_2S(=O){=}NH$$

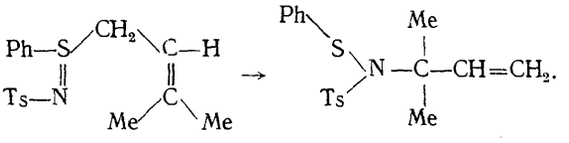
The reaction is stereospecific and in the case of optically active *N*-chlorosulphilimines takes place with 98% retention of configuration at the sulphur atom. The hydrolysis mechanism involves nucleophilic attack by an OH^- group on the sulphur atom to form a transition state which is stabilised through cleavage of a chloride anion.



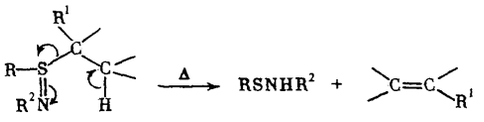
2. Reactions that take place with conversion of the S(IV)=N bond to S(II)–N or S(IV)–N bonds

a) Rearrangement of sulphilimines to sulphenamides

N-Substituted sulphilimines containing an allyl group on the sulphur atom readily undergo various sigmatropic rearrangements, so in many cases they cannot be isolated. One of such types of rearrangement is a [2,3] sigmatropic shift that involves migration of the allyl group from the sulphur atom to the nitrogen atom to form *N*-substituted sulphenamides.[129]



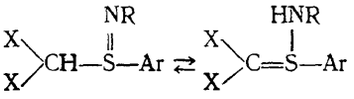
S-Alkylsulphilimines that contain a β-H atom undergo a Pummerer rearrangement on heating, to form sulphenamides and alkenes.[69]



R^1 = H, Me; R^2 = Ar, MeCO.

b) Formation of *S*-aminosulphonium ylides

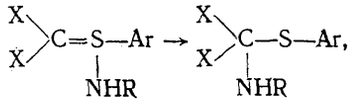
N-Substituted sulphilimines that contain an active α-H atom can undergo a [1,3] sigmatropic rearrangement to form *S*-aminosulphonium ylides



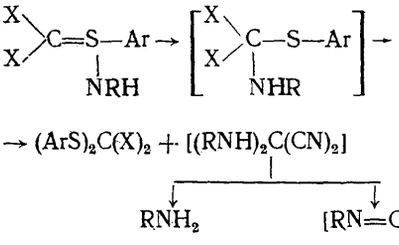
Essentially the rearrangement consists of a prototropic shift in the triad C–S–N, namely an imino–ylide tautomerism, and the possible existence of a given form is determined by the nature of the groups X and R.

In accordance with the principles of an acid-base prototropic equilibrium,[130] a tautomeric equilibrium occurs in those cases where the dissociation constants of both forms differ by a factor of not more than 10^1-10^3. If the difference between the dissociation constants is large, the equilibrium is almost completely displaced towards the form whose dissociation constant is smaller. If we consider with this criterion the C–S–N triad of imino–ylide tautomerism which occurs in a number of *N*-substituted sulphilimines with an active α-H atom, it becomes clear that conversion of the imine form to the ylide form only occurs when the acidity of the CH-form (imine) is comparable to or greater than the acidity of the NH-form (ylide). For the acidity of the CH-form to become equal or greater than the acidity of the NH-form, a strong electron-acceptor effect from groups X is necessary. Therefore, formation of *S*-aminosulphonium ylides was observed[52,53,55,56,109] when strong electron-acceptor groups such as PhCO, MeCO, CN, EtOCO, etc. were introduced as X. In the event that X are weak electron-acceptor groups such as Ph,[131] the prototropic tautomeric equilibrium is completely shifted towards the weakly acidic imine form, namely, a [1,3] sigmatropic rearrangement does not occur.

The stability of *S*-aminosulphonium ylides which are formed as a result of a [1,3] sigmatropic rearrangement of sulphilimines is dependent to a large extent on the nature of groups R on the nitrogen atom. The relatively high stability of *S*-aryl-*S*-(t-butylamino)- and *S*-aryl-*S*-(α-cyanoisopropylamino)sulphonium methylylides has been noted,[109] while *S*-aryl-*S*-(arylsulphonylamino)-sulphonium methylylides[52,53,109] are unstable and undergo further reactions as a result of the migration of the arylsulphonamide group to the carbon atom.



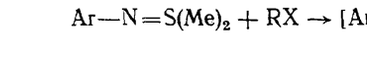
X = PhCO, MeCO; Ar = 4-ClC_6H_4, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$;
R = $PhSO_2$, 4-$MeC_6H_4SO_2$;



X = CN, EtOCO; Ar = 4-ClC_6H_4, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$;
R = $PhSO_2$, 4-$MeC_6H_4SO_2$.

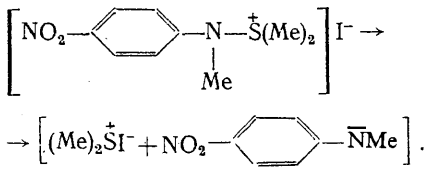
c) Formation of aminosulphonium salts

N-Arylsulphilimines form unstable aminosulphonium salts by reaction with alkylating or acylating agents.[132]

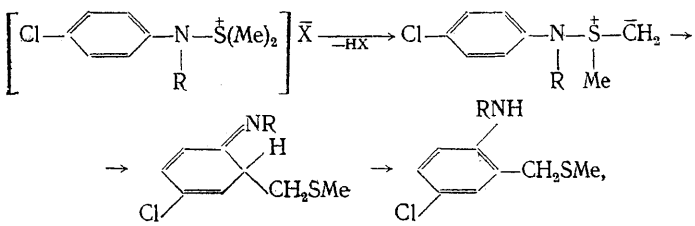


R = Me, X = I; R = EtOCO, X = Cl; R = MeCO, X = $MeCOO^-$;
Ar = *p*-$NO_2C_6H_4$, *p*-ClC_6H_4.

Subsequent conversion of these salts is dependent on the nature of the substituents in the benzene ring of the aryl group and the basicity of X^-. In the case of strong electron-acceptor substituents (such as NO_2) and highly basic X^-, attack by X^- on the positively charged sulphur atom takes place followed by cleavage of the S–N bond



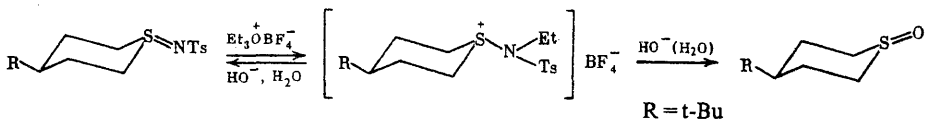
In the case of weak electron-acceptor or electron-donor substituents anion X^- extracts a proton from a MeS group to form an intermediate ylide, which subsequently undergoes an intramolecular sigmatropic rearrangement to give unstable cyclohexadiene derivatives that are converted to more stable benzene derivatives



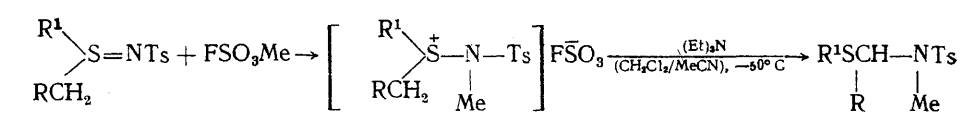
R = Me, X = I; R = MeCO, X = MeCOO; R = EtOCO, X = Cl.

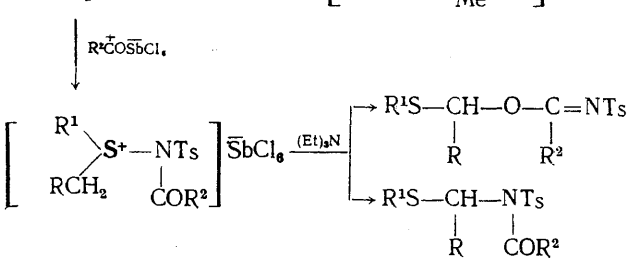
When one of the methyl groups on the sulphur atom is replaced by an ethyl or propyl group, extraction of a proton only occurs from the MeS group, and when it is replaced by a benzyl group the proton is only extracted from the benzyl group, which is correlated with the decrease in acidity in the series $PhCH_2S$ > MeS > $AlkCH_2S$.

N-Arylsulphonylsulphilimines only form aminosulphonium salts in a reaction with highly active acylating and alkylating agents such as oxonium salts ($Et_3\overset{+}{O}BF_4^-$, for example),[129] methyl fluorosulphonate,[133] and complexes of carboxylic acid chlorides with $SbCl_5$.[133] The aminosulphonium salts formed in this case are relatively stable and undergo further reactions only on treatment with mineral or organic bases



R = t-Bu





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

3. Reactions that take place with complete cleavage of the S(IV)=N bond

a) Thermolysis and photolysis of sulphilimines

The composition and nature of the products of thermal decomposition of sulphilimines are determined as a rule by their structure and the conditions of thermolysis. At the same time the thermal destruction processes are often accompanied by various rearrangements, which also contributes to the variety of thermolysis products. This, for example, thermolysis of *N*-acyl-*S*,*S*-diphenylsulphilimines[134] is accompanied by a Curtius rearrangement with the formation of sulphides and isocyanates

$$Ph_2SNCOR \xrightarrow{200\ ^\circ C,\ 2\ h} RNCO + Ph_2S,$$
$$R = PhCH_2,\ PhCH_2CH_2,\ 2,4,6\text{-}(Me)_3C_6H_2,\ Ph.$$

Thermolysis of *N*-*p*-toluenesulphonyl-*S*,*S*-dimethyl- and -diphenylsulphilimines[135] at 300 °C in a current of nitrogen is accompanied by reduction reactions to form mixtures of products, from which Me_2S, $(MeS-)_2$, $(MeS-)_2CH_2$, $4\text{-}MeC_6H_4SO_2NH_2$, PhMe, $(4\text{-}MeC_6H_4S-)_2$, and $4\text{-}MeC_6H_4SSMe$ are isolated. Thermolysis of heterocyclic sulphilimines is often accompanied by ring expansion.[136] The primary products of the photolysis of sulphilimines[137,138] as a rule are the initial sulphides and nitrenes, which, depending on their structure and the type of reaction medium, form various secondary products.

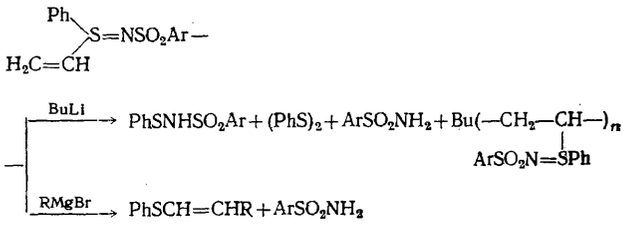
b) Reduction of sulphilimines

Sulphilimines are readily reduced by various reducing agents to give the initial sulphides

$$RR^1S{=}NR^2 \xrightarrow{\text{(reduction)}} RSR^1 + R^2NH_2,$$
$$R = R^1 = Alk,\ Ar;\ R^2 = H,\ Ar,\ AlkSO_2,\ ArSO_2.$$

Phosphorus pentasulphide,[117] titanium tetrachloride with metallic zinc,[121] cysteine,[139] sodium iodide,[140] lithium aluminium hydride,[141] and others have been used as reducing agents. The reaction of *N*-arylsulphonyl-*S*-aryl-*S*-vinylsulphilimines with organolithium and

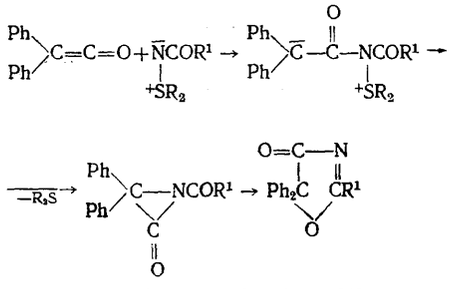
organomagnesium compounds is accompanied by reduction of these sulphilimines[142]



c) Cycloaddition reactions

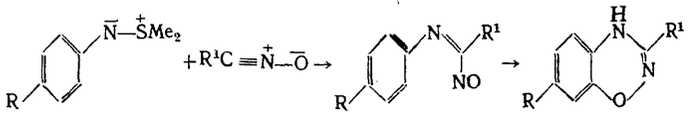
Because of the ylide nature of the S(IV)N=N bond in sulphilimines, they can be used in cycloaddition reactions with compounds containing active double or triple bonds and also systems of cumulated and conjugated double bonds. Meth-Cohn et al.[143] have studied the [4 + 2] cycloaddition of *N*-substituted sulphilimines with compounds containing active C=C bonds. The resulting adducts undergo cleavage to form the highly reactive sulphenylamines R–N=S (R = PhCO, EtOCO, $ArSO_2$). Adducts of the [2 + 2] cycloaddition of sulphilimines to carbon disulphide[114,132] are cleaved to form isothiocyanates, sulphides, and sulphur. Certain cycloaddition reactions only involve the nitrogen atom and groups bonded to it. These reactions are used in the synthesis of heterocyclic compounds. One such reaction is the interaction of *N*-acylsulphilimines with diphenylketene.[144]

The first step in this reaction is nucleophilic attack by the nitrogen atom of the sulphilimine on the electron-deficient carbon atom of the C=O group in diphenylketene followed by cyclisation of the intermediate bipolar compound to form an unstable ethylenimine derivative, which is converted to a more stable 1,3-oxazolin-4-one derivative.

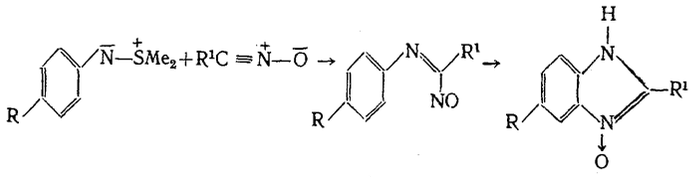


R = Me, Ph; R^1 = Me, CF_3, Ph, $PhCH_2$.

Gilchrist et al.[145] reported that the reactions products from cycloaddition of *N*-arylsulphilimines with nitrile oxides are 1,2,4-benzoxadiazines

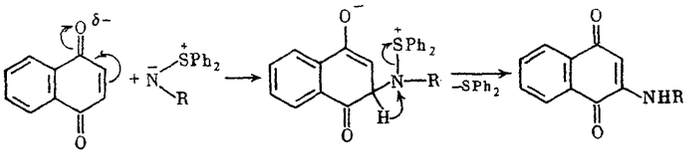


However, according to the results of Shinsaku et al.,[146] cycloaddition does not involve the oxygen atom but the nitrogen atom of the oxynitrile to form benzimidazole *N*-oxides

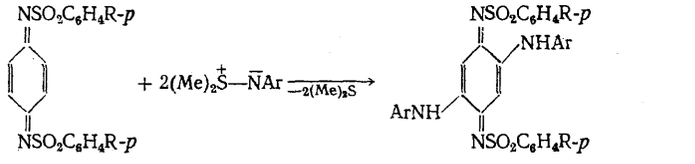


d) Addition to quinoid systems

The high nucleophilicity of nitrogen in *N*-arylsulphilimines can be utilised in their nucleophilic addition reactions to the carbon atoms of a polar system of conjugated bonds of quinones[147] and quinonimines.[148] The proposed mechanism for addition involves nucleophilic attack by the nitrogen atom of the sulphilimine on the terminal carbon atom of the conjugated system of bonds to give an unstable betaine, which is converted as a result of displacement of the sulphonium group by a proton to more stable quinone and quinonimine derivatives.



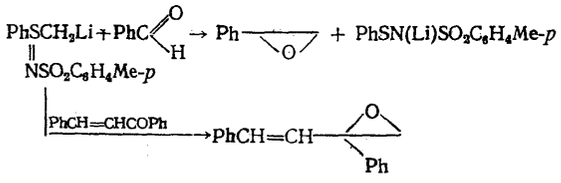
R = $PhCH_2$



R = H, Me; Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$.

e) Transfer of alkylidene groups of *N*-arylsulphonylsulphilimines

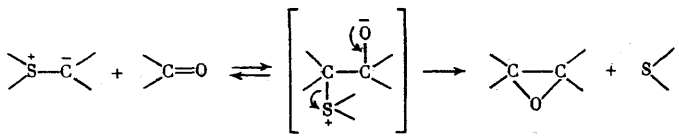
The strong electron-acceptor effect of the arylsulphonylimino group increases the acidity of the α-H atoms of the *S*-alkyl groups, which assists their replacement by an alkali metal atom. Organometallic compounds of this type are used as nucleophilic reagents that transfer alkylidene groups to an electrophilic double bond (such as C=O), forming a three-membered ring.[149] The leaving group whose separation results in the formation of the three-membered ring is a stable *N*-arylsulphonylsulphenamide anion, which also assists this process



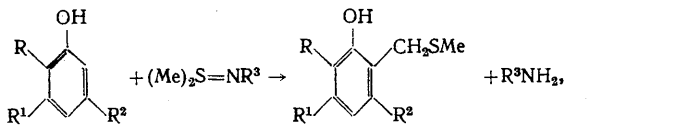
This reaction is characterised by its high stereoselectivity and when other *S*-alkylsulphilimines are used, the resulting 1,2-disubstituted oxiranes mainly have a *trans* structure.[150]

By analogy with the mechanism for transfer of the alkylidene group of sulphur ylides to an electrophilic double bond,[139] the mechanism of this reaction involves the formation of an intermediate

betaine followed by cyclisation through direct substitution at the carbon atom.

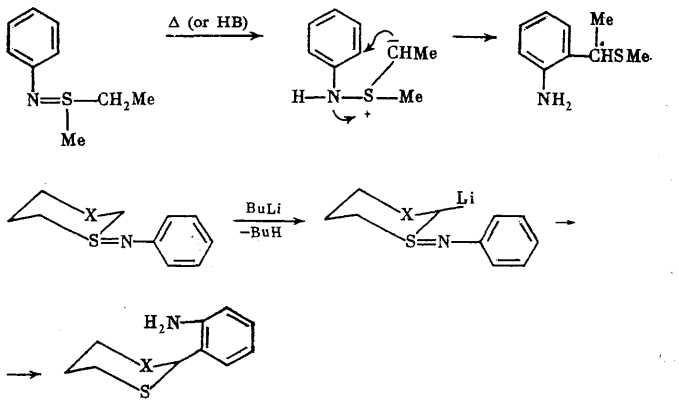


The use of *S,S*-dimethylsulphilimines for the introduction of a methylthiomethylene group into the aromatic ring of phenols has been reported in the literature.[151]



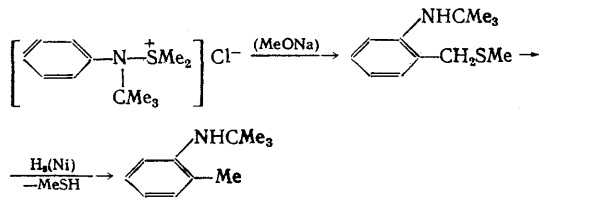
R = Me, OMe; R^1 = H, Me; R^2 = H, Me; R^3 = $ArSO_2$; 2,4-$(NO_2)_2C_6H_3$.

On heating[152] and also by treatment with bases[153] or organolithium compounds,[154] certain *N*-arylsulphilimines undergo a type of Sommelet reaction



X = CH_2S.

Gassman et al.[155] utilised a similar rearrangement of aminosulphonium salts for the *ortho*-alkylation of arylamines.



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Sulphenamides and their derivatives

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ABSTRACT. Information has been presented systematically on the synthesis of sulphenamides and related compounds by reaction of sulphenyl chlorides and sulphur chlorides with amines and carboxylic acid amides; by reaction of chloramines with mercaptans; by transamination of *N*-acylsulphenamides; and by reaction of disulphides with amines. The following chemical reactions of sulphenamides have been examined: reaction with hydrogen halides; with acids and derivatives possessing coordinatively unsaturated atoms; and the addition of sulphenamides to the double bond of carbon disulphide, isocyanates, isothiocyanates and olefins. Data are given on the physical state of sulphenamides and on the region characteristic of the S–N bond vibrations.

The bibliography includes 190 references.

Contents

I. Introduction 832
II. Methods of preparation 832
III. Physical properties 835
IV. Chemical properties 835

I. Introduction

Sulphenamides are important sulphenic acid derivatives which possess a S–N group. The following types of sulphenamide are known: alkyl- and aryl-sulphenamides, *S*-acyl- and *N*-acyl-sulphenamides, sulphenamides derived from the hypothetical sulphoxylic acid, $S(OH)_2$, and thiosulphoxylic acid, $S_2(OH)_2$; and aminosulphenyl chlorides which possess both a S–N bond characteristic of sulphenamides and a S–Cl bond characteristic of sulphenyl chlorides. As the S–N bond is readily cleaved with various reagents, sulphenamides are used in synthetic chemistry for introducing both sulphur and nitrogen functions, affording a variety of sulphides,[1,2] disulphides,[3,4] trisulphides,[5,6] sulphenic acid esters,[7] and other compounds.

Sulphenamides and derivatives are widely used as accelerators in the vulcanisation of rubber,[8–20] in agriculture as pesticides and fungicides,[21–29] for treating the after-effects of radiation sickness, as radio-protecting agents,[30] as polymerisation initiators,[31] and even in rocket technology as spontaneously igniting fuels.[32]

At the present time there is a large volume of data on this subject in foreign publications;[33–37] there is nothing of a review nature with the exception of one article[38] which in part summarises known information.

II. Methods of preparation

Sulphenamides and related compounds are prepared by amination of sulphenyl halides, sulphenic acid esters, and sulphur chlorides with alkyl- and aryl-amines and with amides; they are also obtained by treatment of mercaptans with chloramines, disulphides with amines, from thiosulphonates and alkylsulphenyl thiocyanates with amines, and by other methods.

1. Amination of sulphenyl halides

Zinke was first to prepare sulphenamides in high yield by treatment of sulphenyl chlorides with an excess of secondary amine in chloroform or carbon tetrachloride at low temperature.[33,36,39]

$$R{-}S{-}X + 2HNR^1_2 \rightarrow R{-}S{-}NR^1_2 + HNR^1_2 \cdot HX,$$

$R = Ph,\ O_2N{-}C_6H_4;\ R^1 = Me,\ Et;\ X = Cl,\ Br.$

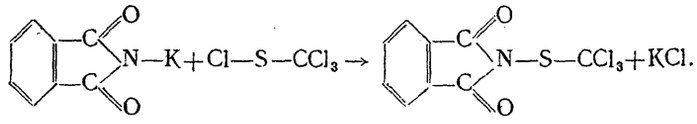
Subsequently, triethylamine[40–42] was used as HCl acceptor in order to economise in the use of the secondary amine. This reaction does not always proceed smoothly with the formation of desired product in high yield. Thus, by treatment of methylsulphenyl chloride with excess of dialkylamine at 60 °C, *gem*-diamines as well as methyldi- and tri-sulphides were obtained together with the desired sulphenamides.[43]

$$Me{-}S{-}Cl + R{-}NH_2 \rightarrow Me{-}S{-}NR_2 + CH_2(NR_2)_2 + Me{-}S_2{-}Me + Me{-}S_3{-}Me,$$

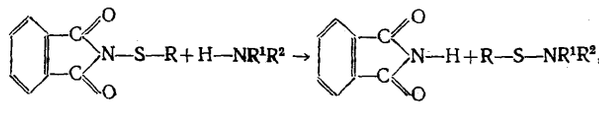
R = Me, Et, *iso*-Pr.

By an analogous route, *N*-methylalkanesulphenanilides were obtained by reaction of the corresponding sulphenyl chlorides with *N*-methylaniline, the only difference being the choice of aqueous base as medium. The desired products were isolated in yields up to 70–80% by extraction and distillation.[44]

This method is recommended for low-molecular weight sulphenyl chlorides, i.e. those with small alkyl (R) groups.[45–47] By such means, *N*-acylsulphenamides are obtained in high yield by reaction of *N*-potassiophthalimide with sulphenyl chlorides.



N-Acylsulphenamides are converted to deacylated sulphenamides by transamination.[48–50]



R = Me, Et, Ph, C_6H_4; R^1 = Me, Et; R^2 = Et, *iso*-Pr.

Isolation of the desired products is facilitated by the use of non-polar solvents in which phthalimide has low solubility.

Those sulphenamides derived from the hypothetical sulphoxylic and thiosulphoxylic acids, referred to usually as thiobisamines and dithiobisamines or diaminosulphides, are obtained in around 90% yield by interaction of sulphur dichloride with secondary aliphatic, cyclic, and *N*-alkylaryl amines in chlorinated hydrocarbon solvents at low temperature or in aqueous basic medium.[51–60]

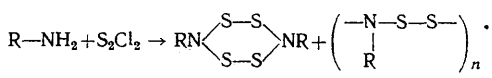
$$4R_2NH \xrightarrow{SCl_2} R_2N{-}S{-}NR_2 + R_2NH\cdot HCl$$
$$4R_2NH \xrightarrow{S_2Cl_2} R_2N{-}S_2{-}NR_2 + R_2NH\cdot HCl$$

R = Me, Et, Pr, Bu, $(CH_2)_5CH$; $R_2 = (CH_2)_2O(CH_2)_2$, $(CH_2)_5$.

Thiobisamines with a HN–S group are obtained by reaction of primary aliphatic and aromatic amines, in particular *tert*-butylamine and *p*-nitroaniline, with sulphur dichloride in ether.[61,62]

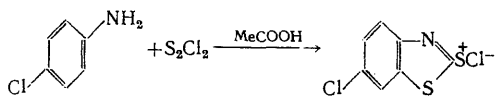
$$R{-}NH_2 + SCl_2 \xrightarrow{ether} RHN{-}S{-}NHR,$$
$$R = p\text{-}NO_2C_6H_4,\ tert\text{-}Bu.$$

It is also reported that primary aliphatic amines with sulphur monochloride produce tetrathiodiamines or polymeric disulphides in 40–60% yield.[63,64]



R = Et, Ph–CH_2, Ph–CH_2CH_2, $C_{12}H_{25}$; n=5–9.

As a rule primary aromatic amines react with sulphur monochloride to give a mixture of products, of which compounds with a C–S bond predominate.[65,66] Thus, by heating *p*-chloroaniline with sulphur monochloride in acetic acid during 3 h, yellow crystals of 6-chloro-1,2-dithiazinium chloride were obtained in 93% yield.[67]



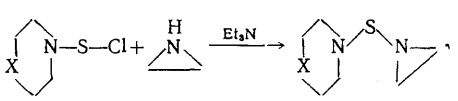
Thiobisamines are obtained in high yield by treatment of metallated secondary amines with sulphur dichloride.[68]

$$R^1R^2NLi + SCl_2 \xrightarrow{-78^\circ C} R^1R^2N{-}S{-}NR^1R^2 + LiCl,$$
$$R^1 = SiMe_3;\ R^2 = Bu,\ iso\text{-}Pr,\ tert\text{-}Bu,\ (CH_2)_5CH.$$

Extremely reactive aminosulphenyl chlorides possessing both sulphenamide and sulphenyl chloride groups are obtained by cleavage of dithiobisamines with chlorine or sulphuryl chloride, as well as by treating thiobisamines with hydrogen chloride.[69,70]

$$R_2N{-}S{-}NR_2 + HCl \rightarrow R_2NSCl + R_2NH\cdot HCl,$$
$$R_2N{-}S_2{-}NR_2 + SO_2Cl_2 \rightarrow 2R_2N{-}S{-}Cl + SO_2,$$
$$R = Me,\ Et,\ iso\text{-}Pr,\ tert\text{-}Bu,\ (CH_2)_5CH;$$
$$R_2 = (CH_2)_2O(CH_2)_2.$$

Aminosulphenyl chlorides are used to prepare thiobisamines with a variety of amino groups. For example, unsymmetrical thiobisamines are obtained by treatment of aminosulphenyl chlorides with ethyleneimine in carbon tetrachloride in the presence of tertiary amine at room temperature.[71]



X = O, S, CH_2.

At the same time it has been reported that on treatment of diethylaminosulphenyl chloride with dimethylamine, and of dibutylaminosulphenyl chloride with dicyclohexylamine, only symmetrical thiobisamines, namely bis(dimethylamino) sulphide and bis(dicyclohexylamino) sulphide, were isolated in 80% yield. It is thought that this reaction proceeds as a result of disproportionation of an initially formed unsymmetrical thiobisamine under the action of hydrogen chloride.[72]

$$R_2NH \xrightarrow[-HCl]{R_2^1NSCl} R_2N{-}S{-}NR_2^1 \xrightarrow[-HNR_2^1]{HCl}$$
$$\rightarrow R_2NSCl \xrightarrow[-HCl]{HNR_2} R_2N{-}S{-}NR_2,$$
$$R = Me,\ (CH_2)_5CH;\ R^1 = Et,\ Bu.$$

Suphenamides phosphorylated on the sulphur atom are obtained by interaction of aminosulphenyl chlorides with dialkyl or trialkyl phosphites in high yield.[73]

$$R_2N{-}S{-}Cl + (R^1O)_3P \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}{-}SNR_2 + R^1{-}Cl,$$
$$R = Et;\ R^1 = Et,\ Pr,\ Bu.$$

The isolation of *S*-dialkylamino dialkyl thiophosphates presents no difficulty because the only side-product of the reaction is a volatile alkyl chloride.

An unstable acetylsulphenamide, which decomposes into sulphur and diethylacetamide, was obtained by reaction of acetylsulphenyl chloride with diethylamine.[74]

$$CH_3\overset{\overset{O}{\|}}{C}{-}S{-}Cl + 2(C_2H_5)_2NH \rightarrow$$
$$\rightarrow CH_3\overset{\overset{O}{\|}}{C}{-}S{-}N(C_2H_5)_2 + (C_2H_5)_2NH\cdot HCl.$$
$$\downarrow$$
$$CH_3C(O)N(C_2H_5)_2 + S$$

A similar result was obtained with piperidine. The oily sulphenamide synthesised from aniline at 3–5 °C decomposed by 50% during 24 h and completely during the course of 3 days.

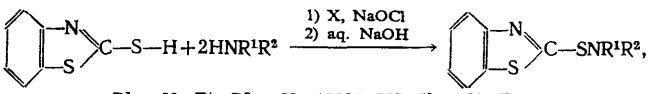
2. Amination of mercaptans with chloramines

Sulphenamides with a free amino group ($-NH_2$) are obtained in yield up to 50% by reaction of mercaptides with chloramine.[75]

$$R{-}S{-}Na \xrightarrow[2)\ aq.\ NaOH]{1)\ NH_2Cl/H_2O} R{-}S{-}NH_2 + NaCl,$$
$$R = pyridyl,\ pyrimidinyl,\ 1,2\text{-}Cl_2C_6H_3,\ O_2N{-}C_6H_4.$$

The reaction was conducted in aqueous basic solution. The sulphenamides were recrystallised from a mixture of petroleum ether and isopropanol. However, if diethyl ether is used as solvent, the corresponding disulphide is formed.

Sulphenamides can also be prepared by the reaction of aromatic mercaptans, notably 2-mercaptobenzothiazoles, with ammonia, or with primary and secondary amines in the presence of hypochlorites, halogens or potassium ferricyanide in aqueous solution.[76–81]



R^1 = H, Et; R^2 = H, $(CH_2)_5CH$; X = Cl, Br, I.

This method is related to the chloramine route since mercaptans and amines react with chlorine or hypochlorite with formation of sulphenyl chlorides and chloramines, following which the former will interact with the amines and the latter with the mercaptides.

N-Acylsulphenamides are also obtained in up to 70% yield by reaction of *N*-chlorosuccinimide and *N*-chlorophthalimide with mercaptans.[82]

$$R^1R^2NCl + HS{-}R^3 \xrightarrow{OH^-} R^1R^2NSR^3,$$

R^1R^2N = succinimido, phthalimido; R^3 = Et, *iso*-Pr, Ph.

3. Amination of disulphides

One of the methods of preparing sulphenamides is based on the interaction of alkyl or aryl disulphides with primary or secondary amines in the presence of silver acetate, silver nitrate or mercuric chloride. The yield of the sulphenamides is 60–80% by this route.[83]

$$R{-}S_2{-}R + 2R^1_2NH + MX \xrightarrow{NaOH} \rightarrow R{-}S{-}NR^1_2 + R{-}S{-}M + R^1_2NH\cdot HX,$$

R = Me, Et, *iso*-Pr, Bu, Ph; R^1 = Me, Et, *iso*-Pr, Bu, Ph;

$MX = AgNO_3$, AgOAc, $HgCl_2$.

It is thought that, initially, a disulphide complex is formed as a result of electrophilic attack of the metal ion; the complex is then decomposed with the formation of sulphenamide as a result of nucleophilic attack by the amine. Reaction is carried out in the following way: equimolar amounts of the disulphide and metal salt in methanol or ethyl acetate are treated with an excess of the amine, the precipitated mercaptide is separated by filtration, and the sulphenamide is isolated from the filtrate by the usual means. Reaction is easiest by using aromatic, as opposed to aliphatic, disulphides, and the yield of the desired sulphenamides is highest. This method is also suitable for preparing sulphenamides with a free NH_2 group if the nucleophile which attacks the sulphur atom is more electron-accepting than 4-chlorophenyl; if the reverse obtains, bis(arylsulphenyl)amines are isolated as the main products.[83]

This method possesses a number of distinct advantages by comparison with the route based on sulphenyl chlorides. Firstly, disulphides are more stable than sulphenyl halides, and secondly the method permits the synthesis of sulphenamides which contain reactive functional groups, such as hydroxyl or a double bond, which are reactive towards sulphenyl chlorides.[45,46]

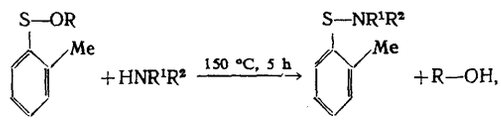
Sulphenamides phosphorylated on the sulphur atom are obtained in high yield by treatment of dithiophosphates with primary and secondary amines.[84]

$$(RO)_2\overset{O}{\overset{\|}{P}}{-}S_2{-}\overset{O}{\overset{\|}{P}}(OR)_2 + 2HNR^1_2 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}{-}S{-}NHR^1 + (RO)_2\overset{O}{\overset{\|}{P}}SH + H_2NR^1,$$

R = Et, *iso*-Pr; R^1 = Me, Et, *iso*-Pr.

4. Amination of arenesulphenates, alkylsulphenyl thiocyanates and thiosulphonates

Sulphenamides are obtained in high yield by amination of arenesulphenates with primary or secondary amines.[85]



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

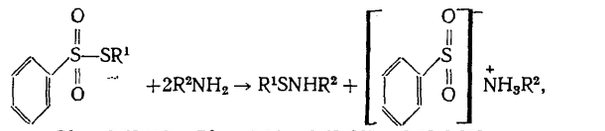
This method is more advantageous than the above-described sulphenyl halide route since sulphenic acid esters are more stable than the corresponding sulphenyl chlorides.

Certain dialkylsulphenamides are obtained by interaction of alkylsulphenyl thiocyanates with a two-fold excess of secondary amine in ether.[86,87]

$$R{-}S{-}S{-}CN + 2R^1_2NH \rightarrow R{-}S{-}NR^1_2 + R^1_2NH\cdot HS{-}CN,$$

R = Et, Pr, Bu; R^1 = Et, Pr, *tert*-Bu.

The possibility of aminating thiosulphonates with amines is exemplified by the amination of 2-nitrophenyl benzenethiosulphonate with aromatic amines. In this case, the corresponding *N*-aryl-2-nitrobenzenesulphenamides are isolated in high yield.[88]



$R^1 = C_6H_4NO_2$; $R^2 = C_6H_5$; $C_6H_4CH_2$, $C_6H_4OCH_2$.

In other cases it is not possible to isolate sulphenamides from a mixture of the corresponding thiosulphonate and aromatic amine.

5. Other methods of synthesising sulphenamides

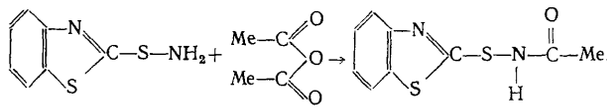
One of these is based on the amination of mercaptides with azides. By this means, treatment of *tert*-butyl or benzyl mercaptan with butyl azidoacetate or azidoformate in the presence of cuprous oxide or cuprous chloride affords the corresponding sulphenamides in 50% yield.[89]

$$R{-}S{-}H \xrightarrow{Cu(I)} Cu{-}S{-}R \xrightarrow[-N_2]{N_3R^1} R^1NHSR + R{-}S_2{-}R + R^1NH_2,$$

R = tert-Bu, $C_6H_4CH_2$; $R^1 = CH_2CO_2Bu$, CO_2Bu.

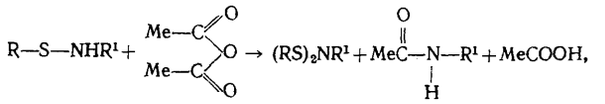
It is proposed[89] that the mechanism of the reaction involves coordination of an intermediate nitrene with the copper atom, followed by insertion of the amino group into the Cu–S bond with formation of sulphenamide, amine and disulphide.

The following method, based on the acylation of sulphenamides with free amino groups, is used for the preparation of acylated 2-benzothiazolylsulphenamides.[90]



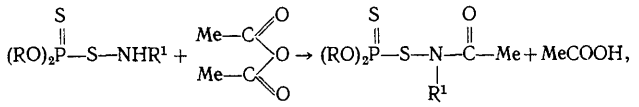
Reaction is conducted in the presence of sodium acetate. In this way, disulphide is formed in addition to acylated product. The desired product was recrystallised from ether. The yield was 30%.

It is known that on acetylation of sulphenamides, the latter are cleaved with the formation of bis-sulphenylamines and the corresponding amide of acetic acid.[91,92]



R = Alk, R^1 = Me.

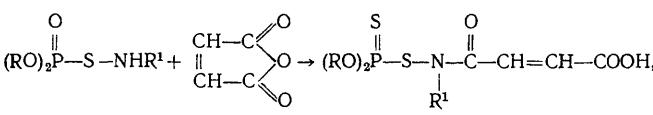
At the same time phosphorylated sulphenamides readily react with acetic anhydride with formation of the corresponding *N*-acetyl derivatives in 72–95% yield.



R = Alk, Ph; R^1 = Me.

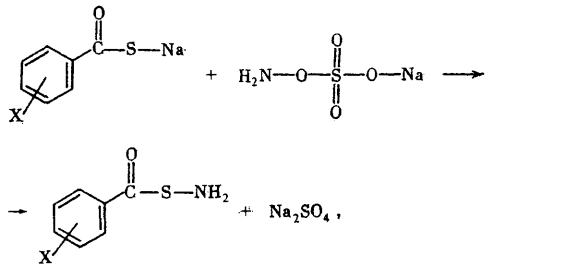
Reaction proceeds at room temperature in the absence of solvent during 30 min, or by vigorous heating of the starting materials up to 100 °C during 2–3 min.

In addition to this, sulphenamides are acylated with maleic anhydride under the same conditions.[93]



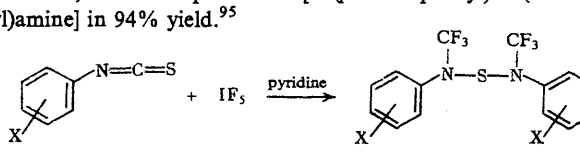
R = Me, Et, *iso*-Pr; R^1 = Me.

One of the methods of preparing *S*-acylsulphenamides is by amination of salts of aromatic thioacids with hydroxylamine-*O*-sulphonates. Reaction is conducted by mixing an aqueous solution of sodium hydroxylamine-*O*-sulphonate with the sodium salt of an aromatic thioacid, followed by filtration of the product and recrystallisation from ether, methylene chloride, chloroform or carbon tetrachloride. The yield was around 90%.[94]



X = Cl, NO_2, Me, H_2NSCO.

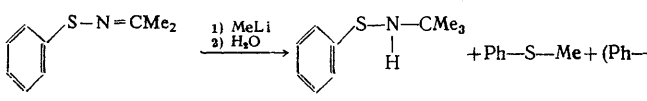
There is a certain interest in the reaction of iodine pentafluoride with phenyl thiocyanates in methylene chloride, leading to the formation of, for example thiobis[*N*-(*p*-chlorophenyl)-*N*-(trifluoromethyl)amine] in 94% yield.[95]



X = Me, Cl, Br, I.

The thiobisamine was isolated from the reaction mixture by column chromatography (eluent: 1 : 1 pentane/methylene chloride).

Sulphenamides can also be obtained by the addition of organometallic compounds to *N*-alkylidenearenesulphenamides, followed by decomposition of the formed products with water. An *S*-phenylsulphenamide was obtained by this route. *N*-Isopropylidenebenzenesulphenamide and methyllithium were used as starting materials.[96]



Reaction was conducted in ether at a temperature around 0 °C; the yield of the sulphenamide was 78%.

III. Physical properties

Sulphenamides and their derivatives exist as liquids or crystalline compounds with clearly defined melting points. The vast majority are colourless, but some are yellow because of impurities. They have an unpleasant smell and are readily soluble in non-polar solvents (benzene, chloroform, methylene chloride, or hexane).[33–38,69,97–100] The S–N bond order in simple methylated mono- and disulphenamides is significantly greater than one. For example, the bond orders for methylthiodimethylamine, Me_2NSMe, and bis(methylthio)methylamine, $MeN(SMe)_2$, and 1.2 and 1.5, respectively.[101] The S–N bond length in unsaturated aliphatic sulphenamides is around 160 pm; for arylsulphenamides it is around 155 pm, and for dithiobisamines the S–S bond length is approximately 195–205 pm. The C–N–S bond angle, around 100°, depends on the nature of the neighbouring atoms and groups.[102–104]

Based on a study of the temperature dependence of the PMR spectra of a series of cyclic and acyclic sulphenamides, it is assumed that inversion at the nitrogen atom is the rate-determining step only for aziridine derivatives.[105,106]

The rotation barrier around the S–N bond in compounds of the type $ArSN(SO_2Ph)Pr$-*iso* is 55–58 kJ mol^{-1}, being dependent on the lone pair interaction, the S–N bond order, and the steric effect of the substituents.[107]

From an X-ray structural analysis, it has been established that the bonds to nitrogen lie almost in the same plane as a result of $p_\pi - d_\pi$ interaction between the sp^2-hybridised nitrogen atom and the electron-donating sulphur atom.[108–110] In the IR spectrum the S–N bond absorbs in the region 640–670 cm^{-1} and 800–900 cm^{-1}.[55,111]

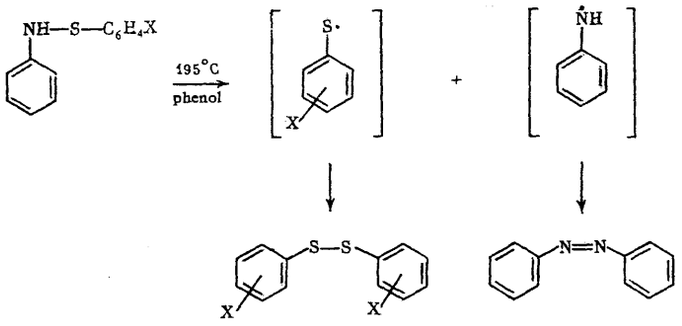
IV. Chemical properties

Sulphenamides and related compounds with a S–N bond are chemically reactive. Characteristically, their reactions proceed by an ionic mechanism, associated with heterolytic cleavage of the S–N bond. The vast majority of these reactions involve nucleophilic substitution or electrophilic addition to a double bond. Reactions of sulphenamides do not normally follow a radical pathway with heterolytic cleavage of the S–N bond. However, such radical reactions do take place in the vulcanisation of rubber, for which sulphenamides serve as accelerators. These reactions have been studied only in rare instances.

1. Thermal decomposition of sulphenamides

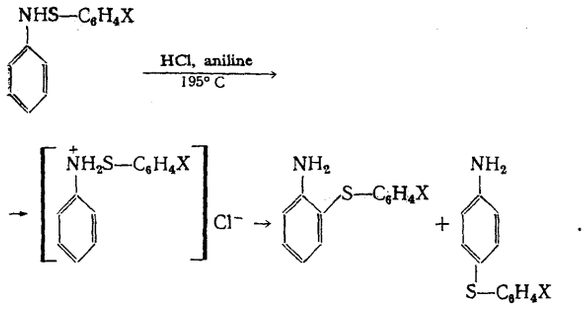
In spite of the widespread use of sulphenamides as accelerators for the vulcanisation of rubber, thermal decomposition of this class of compound has only been studied in the main with arenesulphenamides.[112–114] Thus, on heating sulphenamides to 195 °C, homolysis of the S–N bond takes place with formation of sulphenyl and aminyl radicals, which afford a mixture of disulphide and hydrazobenzene as a result of dimerisation; the hydrazobenzene

then disproportionates to the corresponding azobenzene.[112]

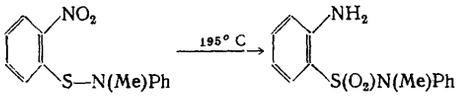


X = Cl, Br, NO_2.

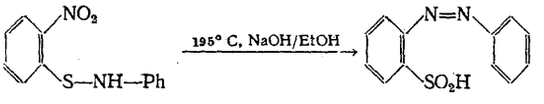
In the presence of acid, a mixture of 2- and 4-aminophenyl aryl sulphide is formed as a result of intramolecular rearrangement of the protonated form of the corresponding sulphenamide.



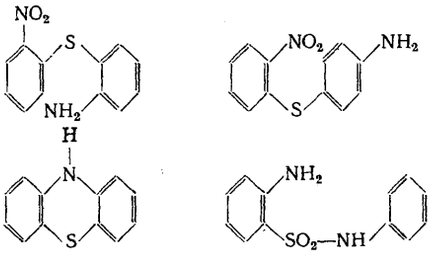
The nature of the solvent has a significant effect on the course of the reaction.[113] Thus, *N*-(2-aminobenzenesulphonyl)-*N*-methylaniline is formed on heating *N*-(2-nitrophenylsulphenyl)-*N*-methylaniline.[115,116]



In ethanolic NaOH, *N*-(2-nitrobenzenesulphenyl)aniline rearranges into an azosulphinic acid.[117]



A mixture of 2- and 4-aminophenyl 2-nitrophenyl sulphide, phenothiazine, and *N*-(2-aminobenzenesulphonyl)aniline was obtained by heating *N*-(2-nitrobenzenesulphenyl)aniline to 195 °C for 15 h in aniline.[118]



Alkylsulphenamides are more unstable than arylsulphenamides. The thermal stability decreases where a neighbouring group exerts an anchimeric effect on S–N bond cleavage (for example, in the presence of an acyl group), and as the basicity of the sulphenamide increases.[38]

2. Hydrolysis

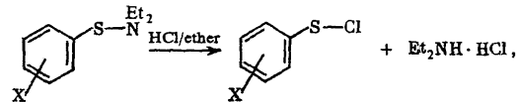
There are no data on the hydrolysis of sulphenamides. Evidently, this is explained by the fact that hydrolysis leads to sulphenic acids which in the large majority of cases are unstable.[33,119] However, a study of the hydrolysis of thiobisamines and dithiobisamines with dilute HCl has been made. Thus it has been shown that hydrolysis of these derivatives affords a mixture of sulphur dioxide, sulphur, hydrogen sulphide and the corresponding amine.[120]

$$RN_2—S_x—NR_2 \xrightarrow{H_2O+HCl} SO_2+H_2S+S+R_2NH,$$
$$R = Me, Et, iso\text{-}Pr;\ x = 1, 2.$$

It is considered that reaction proceeds via sulphur chlorides which then undergo hydrolysis. Sulphenamides and related compounds are comparatively stable in cold aqueous and aqueous basic media, so that they can be prepared in the latter medium by reaction of sulphenyl chlorides with amines or from chloramines and mercaptides; sulphenamides may also be isolated from complexes by treatment with aqueous base.[37,121]

3. Reaction with hydrogen halides

Sulphenamides are readily cleaved with hydrogen halides with formation of sulphenyl halides in high yield.[122–133] The best results are achieved if HCl gas is passed through an ethereal solution of the sulphenamide.[122–130]

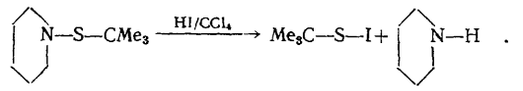


X = H, NO_2.

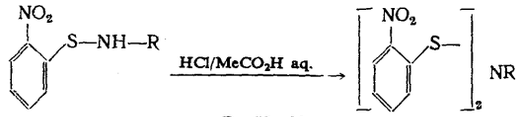
In this way, *o*-nitrobenzenesulphenyl chloride was obtained by using *o*-nitrobenzenesulphenamide. The yields of sulphenyl halide are lower if the sulphenamides are treated with HBr or HI.[127,131] For example, sulphenyl bromides were obtained by treating the corresponding sulphenamides with ethereal HBr at *ca.* 0 °C;[127]

$$R—S—NHR^1 \xrightarrow{HBr/ether} R—S—Br+HNRR^1,$$
$$R = tert\text{-}Bu,\ NO_2C_6H_4;\ R^1 = Me, Et, iso\text{-}Pr,$$

and *tert*-butylsulphenyl iodide and piperidine were obtained by treatment of a solution of *N*-*tert*-butylthiopiperidine with aqueous HI in carbon tetrachloride.[131]

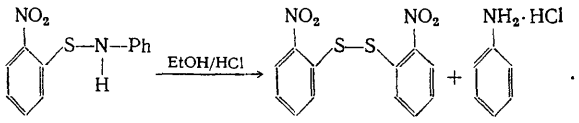


The yields of sulphenyl chlorides are lower if the sulphenamides are cleaved with concentrated hydrochloric acid.[40,134–136] It is also reported that if the derived sulphenyl chlorides are unstable, the corresponding disulphide is obtained; and by heating sulphenamides with dilute hydrochloric or acetic acid, sulphenimides are formed.[136]



R=H, Me.

Only disulphide and aniline hydrochloride are formed on heating the corresponding sulphenanilide in ethanol or in dilute hydrochloric acid.[134,137–139]



Thio- and dithio-bisamines are cleaved at the S–N bond in the same way as sulphenamides by action of anhydrous HCl with the formation of sulphur chlorides and amine salts.[70,120]

$$R_2N{-}S_n{-}NR_2 + 4HCl \xrightarrow{\text{ether, 0 °C}} S_nCl_2 + 2R_2NH\cdot HCl,$$
$$R = Me, Et, Bu;\ n = 1, 2.$$

The reactions of sulphenamides with anhydrous HF have also been studied with a view to preparing sulphenyl fluorides, RSF, as a new class of compound.[140] However, on treatment of trichloromethylsulphenyldiethylamine with HF, the following were isolated from the reaction mixture: dichlorofluoromethylsulphenyl chloride, $CFCl_2SCl$, difluorochloromethylsulphenyl chloride, CF_2ClSCl, and products derived by cleavage of the S–C bond, namely trichlorofluoromethane and trichloromethylsulphenyl chloride.

$$Cl_3CSNEt_2 \xrightarrow{\text{HF, } -78°\text{C}} CFCl_2SCl + CF_2ClSCl + CCl_3F + CCl_3CSCl.$$

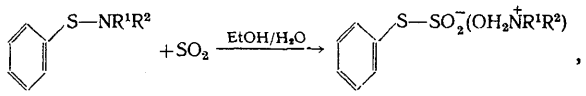
The formation of sulphenyl chlorides in this reaction is evidently a consequence of an initial replacement of chlorine at the carbon atom; the resulting hydrogen chloride then cleaves the S–N bond of the sulphenamide leading to formation of the sulphenyl chloride. Trifluoromethylsulphenyldiethylamine has been used as substrate to prevent this complication. In this case, only cleavage of the S–N bond was noted on heating to 90 °C.

On analysing the mass spectrum of the mixture, an ion of mass 158, corresponding to CF_3SF_3, was detected. Thus, in no case is there formation of sulphenyl fluoride on treatment of the corresponding sulphenamide with anhydrous HF.

The ready cleavage of sulphenamides at the S–N bond on treatment with hydrogen halides has been applied both to the removal of *N*-sulphenyl protective groups from amino-acids in peptide synthesis,[128,129,141–143] and to the preparation of certain sulphenyl halides.[122,126,127,130]

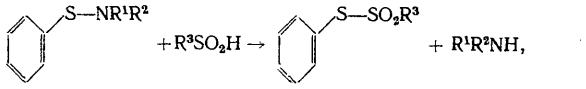
4. Reactions with sulphurous acid, sulphinic acids, dialkyl phosphites and monoalkyl phosphinites

Sulphenamides readily react with sulphur dioxide in an aqueous ethanolic medium during 1 h at 60 °C with the formation of Bunte salts in high yield up to 70%.[144]



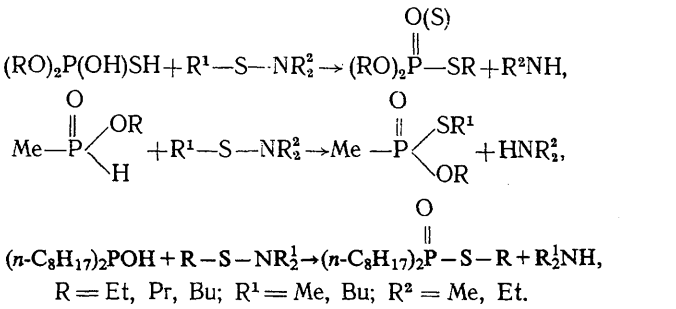
R^1 = Me, Et, *iso*-Pr; R^2 = Me, Et.

Sulphenamides react in a similar manner with sulphinic acids under the same conditions. In this case thiosulphonic acid esters are obtained.[29,145]



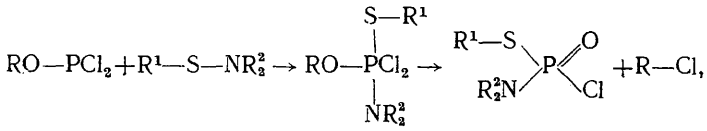
R^1, R^2 = Alk; R^3 = Alk, Ar.

Sulphenamides react with dialkyl phosphites, thiophosphites, phosphinous acid monoesters and dialkylphosphine oxides with the formation of thiolphosphates, thiolphosphonates and thiolphosphinates in 75–95% yield.[146]



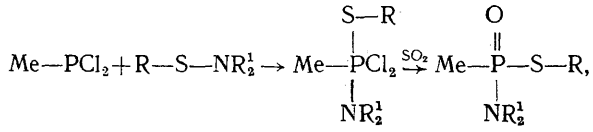
R = Et, Pr, Bu; R^1 = Me, Bu; R^2 = Me, Et.

Sulphenamides react similarly with phosphonous and phosphorous acid chlorides and with phosphonous anhydrides. For example, *S*-alkyl thiophosphoramidochloridates are obtained by interaction of alkyl phosphorodichloridates with sulphenamides.



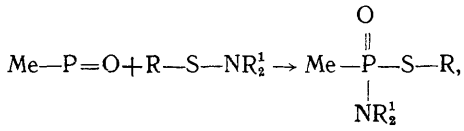
R = Me; R^1 = Bu, *tert*-Bu; R^2 = Me, Et.

Sulphenamides react with methyldichlorophosphine to afford intermediate phosphoranes which are converted to the corresponding *S*-alkyl thiophosphonamidates on treatment with sulphur dioxide.



R = Bu, *tert*-Bu; R^1 = Me, Et.

Methylphosphonous anhydride, like the corresponding dichlorophosphine, also yields *S*-alkyl thiophosphonamidates.



R = Bu, *tert*-Bu; R^1 = Me, Et.

5. Reactions with hydrogen sulphide and mercaptans

Thio- and dithio-bisamines react comparatively smoothly with hydrogen sulphide to give trisulphides from the former, and polysulphides from the latter.[122]

$$RN_2{-}S_n{-}NR_2 + H_2S \rightarrow H{-}S{-}S_n{-}SH + R_2^2N^+H_2HS_4^-,$$
$$R = Me, Et, iso\text{-}Pr, tert\text{-}Bu;\ n = 1-4.$$

Aryl- and alkyl-sulphenamides react easily with mercaptans to yield the corresponding disulphide and amine, but the same reaction with *N*-acylsulphenamides is less facile. Thus, at room temperature or on cooling, arylsulphenamides are cleaved by mercaptans in dimethylformamide, hexane, or pyridine, thereby providing

disulphides and amines in high yield.[129]

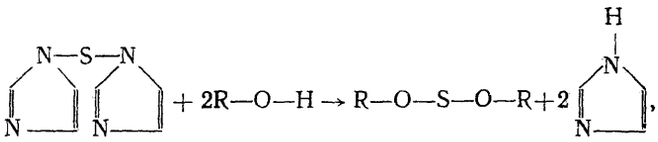
$$R{-}S{-}NR^1R^2 + H{-}S{-}R^3 \xrightarrow{DMF} R{-}S{-}S{-}R^3 + HNR^1R^2,$$

R = Me, Et, Ph, $O_2NC_6H_4$; R^1 = Me, Et, Ac; R^2 = H, Me, Et; R^3 = Et, Pr, Ph.

This procedure is also followed for the removal of sulphenamide protecting groups in peptide synthesis.

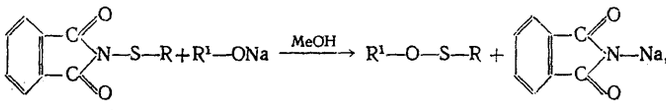
6. Reactions with alcohols

Thiobisamines react with alcohols in pentane at low temperature with the formation of sulphoxylic acid esters, as exemplified by the converison of bis(1-imidazolyl) sulphide.[147,148]



R = Et, Bu, *tert*-Bu, *iso*-Pr.

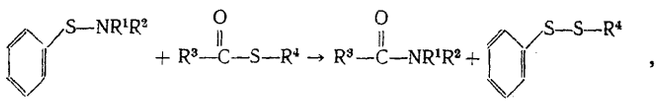
N-Acylsulphenamides interact with alkoxides in methanol at 40–50 °C to give the corresponding sulphenic acid esters in 50–70% yield.[149]



R = Bu; R^1 = Me, Et, *iso*-Pr, *tert*-Bu.

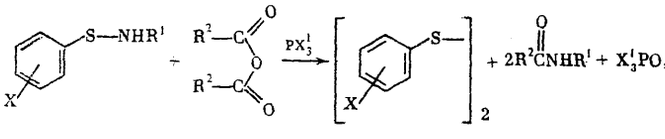
7. Reactions with carboxylic acids and their derivatives

Sulphenamides are efficient reagents for the conversion of thiolcarboxylic acid esters, carboxylic acid anhydrides and acyl chlorides to the corresponding amides. Reaction proceeds under mild conditions in the presence of phosphorus(III) compounds, the amide yield sometimes reaching 95%.[150–153]



R^1 = Me, Et, Bu, Pr; R^2 = Me, Et, Bu, *iso*-Pr; R^3 = Me, Et, Bu, Ph; R^4 = Ph, $O_2NC_6H_4$.

In the case of carboxylic acid anhydrides, amination of both acyl groups takes place, the phosphorous(III) reagent serving as catalyst and, at the same time, functioning as acceptor of oxygen.[153]

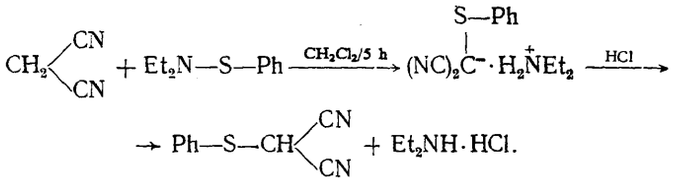


R^1 = Ph; R^2 = Me, Et, Ph; X = H, NO_2; X^1 = Ph, OEt.

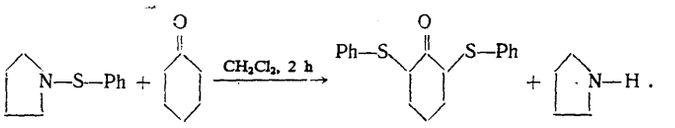
The activating effect of the catalyst is explained by an initial attack on the sulphur atom of the sulphenamide, which ultimately produces an active phosphonium salt. Thus, the catalyst serves to polarise the S–N bond, and consequently effects its cleavage.[152]

8. Reactions with CH-acids

Certain sulphenamides have proved effective for the sulphenylation of compounds possessing active methylene groups.[2,154–157] Thus, the diethylammonium salt of phenylthiomalononitrile was isolated in 85% yield by stirring equimolecular amounts of *N,N*-diethylphenylsulphenamide and malononitrile in methylene chloride during 5 h at room temperature.[2] Phenylthiomalononitrile was obtained by treatment of the salt with hydrogen chloride.

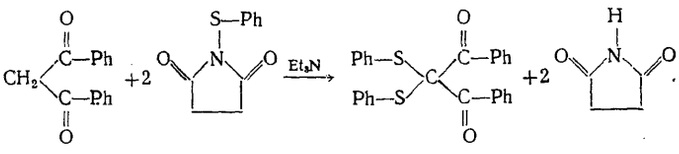


2,6-Bis(phenylthio)cyclohexanone was obtained in high yield by interaction of 2 moles of *N*-phenylthiopyrrolidine with 1 mole of cyclohexanone in methylene chloride at room temperature during 2 h.[2]



It should be pointed out that not every sulphenamide is suitable for sulphenylation. Referring to the above reaction, it is not possible to sulphenylate cyclohexanone by using *N,N*-diethylphenylsulphenamide.

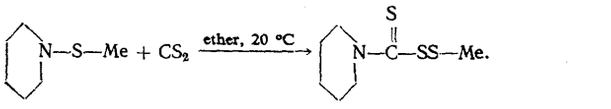
For bis-sulphenylation of methylene groups with *N*-acylsulphenamides, it is recommended that the reaction be conducted in the presence of basic reagents. Thus, bis(phenylthio)dibenzoylmethane was obtained in 50% yield by treatment of 1 mole of dibenzoylmethane with 2 moles of *N*-phenylthiosuccinimide in the presence of 2 moles of triethylamine in methylene chloride at room temperature.[154]



In this case, a succinimide-amine complex is formed together with the triethylammonium salt of the monosulphenylated derivative, which reacts with the sulphenamide to produce bis(phenylthio)-dibenzoylmethane.

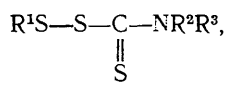
9. Addition of sulphenamides to multiple bonds

The reaction of a sulphenamide with carbon disulphide is typical of a sulphenamide addition across a multiple bond, wherein two hetero-functions are incorporated as a result of the familiar S–N bond cleavage. Thus, methyl *N*-cyclopentamethylenetrithiocarbamate was obtained in more than 80% yield by interaction of an ethereal solution of *N*-methylthiopiperidine with carbon disulphide at room temperature over 5 min.[158,159]



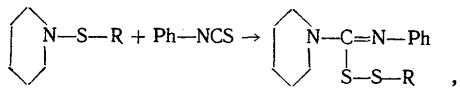
It is suggested that reaction is facilitated by coordination of carbon disulphide to the lone pair on nitrogen, with subsequent insertion into the S–N bond to provide the trithiocarbamate.

However, if the substituent on the sulphur atom of the sulphenamide is strongly electron-accepting, reaction with carbon disulphide does not take place. The following trithiocarbamates have been obtained by this method:



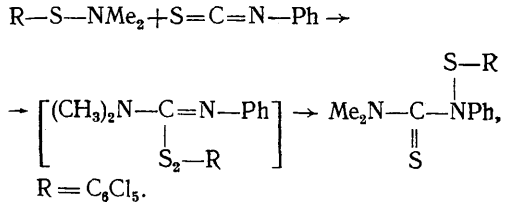
R^1 = Me, Et, *tert*-Bu, allyl;
R^2 = Me, Et, $(CH_2)_5CH$; $R^1R^2 = (CH_2)_4O$.

Sulphenamides react in the same way with isothiocyanates.[40,160,161] It was found that *S*-alkylthio-*N*-cyclopentamethylene-*N'*-phenylisothioureas are formed by interaction of *N*-*tert*-butylthio- or *N*-ethyl-thio-piperidine with phenyl isothiocyanate as a result of addition across the C=S bond, as takes place with carbon disulphide.



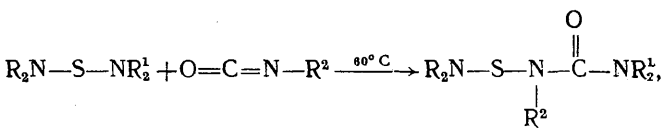
R = Et, *tert*-Bu.

The reaction of sulphenamides with isothiocyanates sometimes leads to the formation of thiourea derivatives rather than *S*-(alkylthio)isothioureas.[160] It would appear that in this case it is the C=N bond of the isothiocyanate which is cleaved, not the C=S bond as in the above case. However, mechanistically this is not true. In fact, in the initial stage of the reaction, the sulphenamide adds across the C=S bond with the formation of the corresponding *S*-(organothio)isothiourea, which subsequently isomerises to the thiourea derivative.



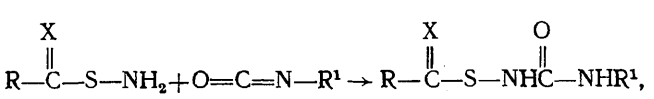
R = C_6Cl_5.

Thiobisamines add to isocyanates by cleavage of the C=N bond with the formation of *N*-substituted ureas in 80–90% yield.[160]



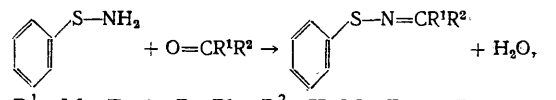
R = Et; $R^1_2 = (CH_2)_5$, $(CH_2)_4O$; R^2 = Me, Ph.

S-Acylsulphenamides react with isocyanates by addition to the N=C bond, as in the above case. For example, urea derivatives are obtained in 70–80% yield by allowing the reaction mixture to stand in acetone for 20 h.[160]



R = Ph, 3,4-$Cl_2C_6H_3$; R^1 = Me, Ph, ClC_6H_4; X = O, S.

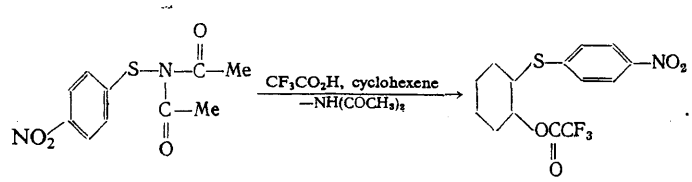
Sulphenamides with a free amino group react with aldehydes and ketones in the same manner as primary amines, affording the corresponding aldimines and ketimines.[162,163]



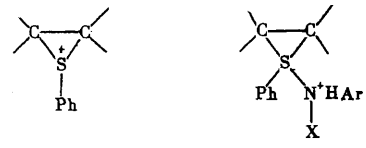
R^1 = Me, Et, *iso*-Pr, Ph; R^2 = H, Me, Et, *iso*-Pr.

Sulphenamides with a tertiary amino group (NR_2) do not react with aldehydes and ketones.

The possibility of adding sulphenamides to a double bond with the participation of an external nucleophile was shown for the first time in 1981, for example, in the reaction of *N*,*N*-diacetyl-*p*-nitrophenylsulphenamide with cyclohexene in the presence of trifluoroacetic acid.[164]

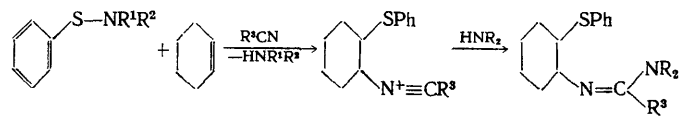


A sulphenium ion is formed as a consequence of two factors: the presence of two electron-accepting acyl groups in the sulphenamide, and the presence of a strong acid in the medium. The ion thus formed adds to the olefin producing an episulphonium complex which is cleaved by the trifluoroacetate ion to provide a *trans*-adduct: *p*-nitrophenyl *trans*-2-(trifluoroacetoxy)cyclohexyl sulphide in the above example. Thus, a sulphenium cation, or an ammonium ion in which the S–N bond is significantly polarised (a partial positive charge developing on the sulphur atom), interacts with the olefin to form either an episulphonium ion (I) or a covalently bonded sulphurane (II), which is subsequently cleaved with the nucleophile.



(I) (II)

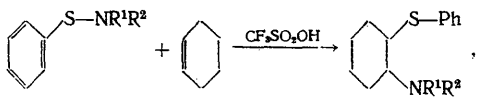
The formation of an episulphonium ion is considered more likely. With a nitrile as the external nucleophile, addition across the multiple bond takes place on activation of the sulphenamides with trifluoromethanesulphonic acid.[165–169] In this way, amidines are obtained in high yield.[165]



R=Me, Et; R^1, R^2=$(CH_2)_5CH$, $(CH_2)_2O(CH_2)_2$; R^1=H; R^2=Bu; R^3=Ph.

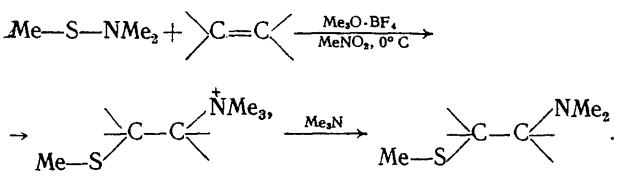
If the reaction of a phenylsulphenamide with cyclohexene in methylene chloride is allowed to proceed in the presence of an external nucleophile as well as trifluoromethanesulphonic acid as

activating agent, then aminosulphides are obtained in high yield.[170–172]

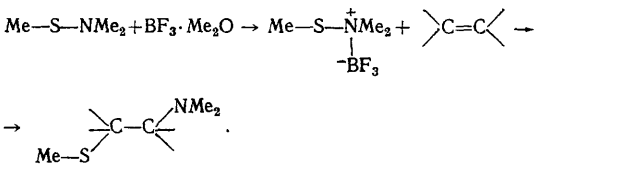


R^1, $R^2=(CH_2)_5$, $(CH_2)_2O(CH_2)_2$; $R^1=H$; $R^2=$ *tert*-Bu.

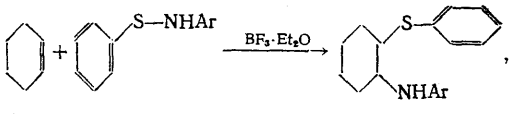
Trimethyloxonium fluoroborate or boron fluoride etherate may also serve as activator. In the presence of the former, sulphenamides interact with olefins in nitromethane to give a β-(methylthio)alkyltrimethylammonium salt which is converted into an amine on treatment with trimethylamine.[173]



In the presence of boron fluoride etherate, reaction of a sulphenamide with an olefin yields a trifluoroboratoammonium salt from which an aminoalkyl sulphide is liberated on treatment with base.

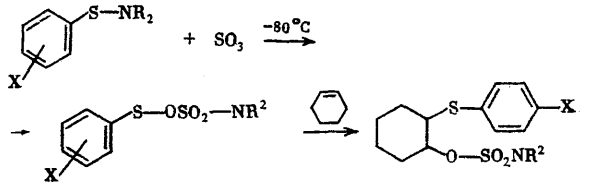


The addition of phenylsulphenamides to cyclohexene in benzene containing a 50% excess of boron fluoride at room temperature leads, stereospecifically, to the corresponding *trans*-adduct in 50 to 90% yield.[174]



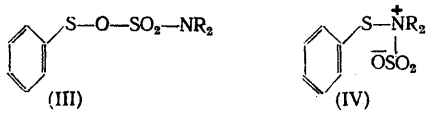
Ar=4-$NO_2C_6H_4$, 4-ClC_6H_4, 4-MeC_6H_4, 4$MeOC_6H_4$, 3$MeOC_6H_4$.

It has been shown that *N,N*-diethylphenyl- or *N,N*-diethyl-*p*-nitrophenylsulphenamide in the presence of sulphur trioxide also add stereospecifically to cyclohexene, affording *trans*-1,2-disubstituted cyclohexanes in high yield.[175–178]



R = Et; X = H, NO_2.

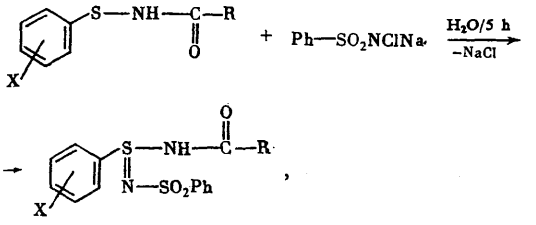
It is proposed that, initially, the sulphenamide and sulphur trioxide form an intermediate, (III) or (IV), from which the electrophilic moiety is derived.[175]



(III) (IV)

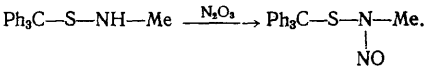
10. Other reactions

It has been reported that *N*-acylarylsulphenamides undergo sulphonylimination with sodium *N*-chlorobenzenesulphonamide (Chloramine B). Thus, as with thioethers, Chloramine B interacts with *N*-acylarylsulphenamides in aqueous medium to give the corresponding *N*-acylaryl(sulphonylimido)sulphinamides in 40–80% yield.[179–181]

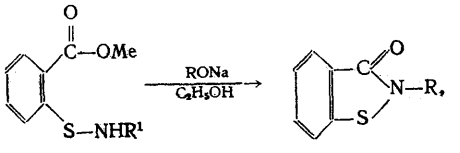


R = Me, Ph; X = H, NO_2.

N-Monoalkylsulphenamides react with nitrogen oxides (N_2O_3) in the same manner as secondary amines to provide nitrososulphenamides in 50–55% yield.[137]

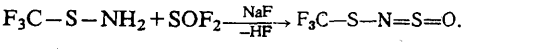


N-Monoalkylphenylsulphenamides which possess an *o*-carbalkoxy group cyclise by intramolecular acylation to 1,2-benzoisothiazol-3-ones.[182]

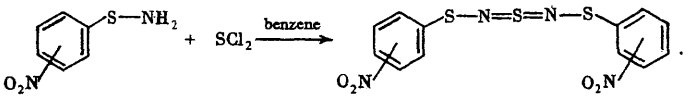


R=Alk; R^1=$PhCH_2$, Pr, CH_2CH_2OH, Ph, MeOPh.

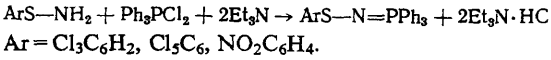
Sulphenamides with a free amino group react with thionyl fluoride, sulphur dichloride and triphenylphosphine dichloride. Thus, in the first case, trifluoromethylthionylimine is obtained by interaction of trifluoromethylsulphenamide with thionyl fluoride in the presence of sodium fluoride at 20 °C.[183]



In the second case, *N,N'*-bis(*p*-nitrobenzenesulphenyl)sulphur diimide is formed in 70% yield by treatment of *p*-nitrobenzenesulphenamide with sulphur dichloride in benzene at room temperature.[184]



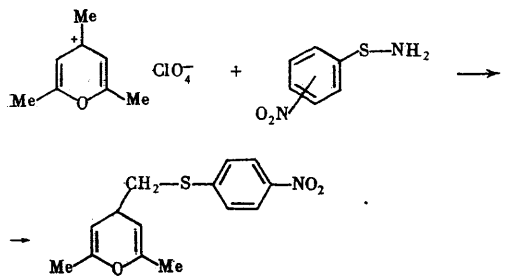
In the third case, boiling a solution of arylsulphenamide and triphenylphosphine dichloride in carbon tetrachloride for 30 min in the presence of tertiary amine affords the corresponding phosphazo compound in 50–90% yield.[185]



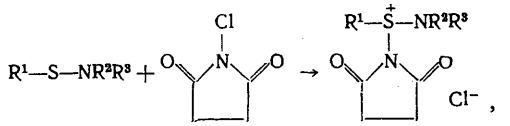
Ar=$Cl_3C_6H_2$, Cl_5C_6, $NO_2C_6H_4$.

It has been shown that a thioether is formed in 80% yield by interaction of *p*-nitrobenzenesulphenamide with a 2,4,6-trimethyl-

pyrylium salt which possesses an active methyl group at the 4 position.[185]

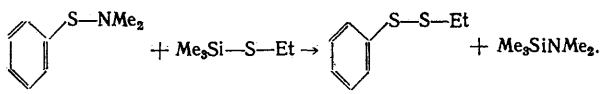


Succinimidosulphonium salts are obtained in 80–90% yield by reaction of sulphenamides with *N*-chlorosuccinimide in methylene chloride at 0 °C.[186]

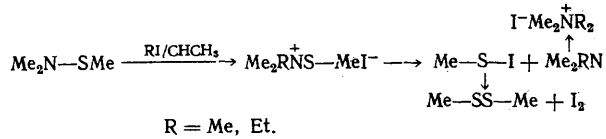


R^1 = Me, Et, Ph; R^2 = Me, $PhCH_2$; R^3 = Me, $PhCH_2$.

It has been reported that unsymmetrical disulphides are obtained by reaction of sulphenamides with alkyl- or aryl-thiosilanes. Thus, ethyl phenyl disulphide was isolated in 47% yield from the reaction of *N,N*-dimethylphenylsulphenamide with ethylthiotrimethylsilane in hexane at 0 °C.[4]

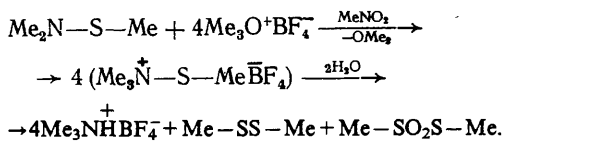


Sulphenamides are alkylated with alkyl iodides with the formation of unstable salts.[4,187–190] Thus, dimethyl disulphide and a tetraalkylammonium iodide were isolated in almost quantitative yield by treatment of *N,N*-dimethylmethanesulphenamide with a solution of methyl or ethyl iodide in chloroform. The reaction proceeds via an unstable alkylthioammonium salt which disproportionates into the disulphide, iodine and the tetraalkylammonium salt.



R = Me, Et.

Furthermore, methylation of sulphenamides with trimethyloxonium fluoroborate in nitromethane also leads to the formation of an alkylthioammonium salt which is very sensitive to moisture and decomposes into the corresponding disulphide, thiosulphonate and trialkylammonium fluoroborate.[190]



A similar reaction takes place on treatment of a thiosulphonium fluoroborate with a tertiary amine in nitromethane.

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Deoxygenation of coordinated and free sulphoxides

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ABSTRACT. The deoxygenation reactions of coordinated R_2SO molecules (R = Alk, Ar) that occur with the formation of dialkyl and diaryl sulphide complexes are examined. Reduction reactions of free sulphoxides involving metal complexes and ions have been classified. It is shown using specific examples which synthetic problems can be solved with the use of different deoxygenating agents and reagent systems.

The bibliography includes 126 references.

Contents

I.	Introduction	844
II.	Reactions involving hydrohalic acids	844
III.	Conversion reactions of DMSO in systems of the type M–DMSO–RX	845
IV.	Reaction between inner-sphere DMSO in Pt(II) complexes and $SOCl_2$	845
V.	Deoxygenation of sulphoxides coordinated to Pt(II) with the reagent system PCl_5–ROH	846
VI.	Conversion of sulphoxides on treatment with metal ions in lower oxidation states	847
VII.	Reactions of sulphoxides with Mo(IV) complexes	847
VIII.	Processes involving metal ion–reducing agent systems	848
IX.	Reduction of sulphoxides with carbonyl or carbene ligands in complexes	848
X.	Processes that occur in sulphoxide phosphine complexes	849
XI.	Other deoxygenation reactions of sulphoxides	849
XII.	Conclusion	850

I. Conclusion

The considerable interest in sulphoxides is in many respects governed by the role which they have played and still play in the development of theoretical concepts in chemistry and also in resolving a number of practical problems. One of the most important properties of R_2SO molecules is their ability to undergo deoxygenation to give sulphides R_2S. The number of publications on this topic is quite considerable.[1–9] The majority of these studies are devoted to the deoxygenation of free sulphoxide molecules, whereas the reduction reactions of coordinated R_2SO molecules have been examined only briefly[7–9] or not considered at all. On taking into account the fact that deoxygenation of coordinated sulphoxides is of theoretical interest in relation to studies on the reactions of coordinated ligands and also that reduction reactions of inner-sphere R_2SO molecules can be of significance for the preparation of complexes that incorporate sulphides R_2S, we decided to compensate for this omission especially since a considerable amount of factual data on the reduction reactions of R_2SO molecules in metal complexes has appeared during the last 8–10 years.

II. Reactions involving hydrohalic acids

The first studies on the deoxygenation of free sulphoxides using HX (X = Cl, Br, I) were carried out at the beginning of the 20th century.[10–13] It was noted in a review article[5] that in general the reduction reactions of this type may be represented by the following equation:

$$R{-}S(O){-}R' + 2HX \rightarrow R{-}S{-}R' + X_2 + H_2O.$$

It was established also that the intermediate in this process is the halosulphonium salt $[R{-}\overset{+}{S}(X){-}R']X^-$, which, depending on X and also the nature of R and R', is either readily reduced to the corresponding sulphide RSR' or decomposes to form a mixture of products, amongst which RCl and RSH in particular have been identified.

Deoxygenation of dimethyl sulphoxide (DMSO) in a metal complex was carried out for the first time in 1968 [14] in a study of the reaction between $[Pt(DMSO)_2Cl_2]$ and hydrochloric acid. From IR spectroscopic data and elemental analysis, the reaction product was identified as $[Pt(DMS)_2Cl_4]$, where DMS = dimethyl sulphide. It was proposed[14] that the process takes place according to the following overall equation:

$$[Pt(DMSO)_2Cl_2] + 4HCl \rightarrow [Pt(DMS)_2Cl_4] + Cl_2 + 2H_2O.$$

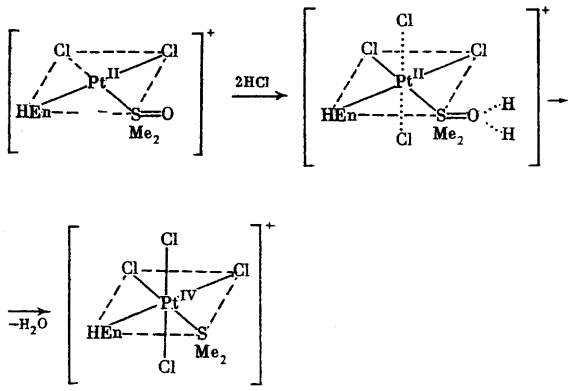
It was noted, however, that this reaction is accompanied by two side reactions and the final Pt(IV) complex is contaminated with unidentified products.

In the same year an article was published[15] in which there was a specific description of the reaction between $PdCl_2$ and tetramethylenesulphoxide (TMSO) in acetone saturated with anhydrous HCl. It was noted that the reaction of $PdCl_2$ with TMSO takes place quite rapidly and gives the complex $[Pd(C_4H_8S)_2Cl_2]$ with coordinated tetramethylenesulphide molecules. Unfortunately, Meek et al.[15] did not study or discuss the mechanism of this reaction.

In the 1970s the chemistry of sulphoxide complexes started to undergo rapid development.[7,16–19] However, only two reports appeared in the literature on the deoxygenation of R_2SO molecules in complexes. Thus, it is noted by Braddock et al.[20] that compounds of the type $[Pt(Am)_2(DMSO)Cl]Cl$ (Am = amine) in aqueous perchloric acid ($[HClO_4] > 1.0$ mol^{-1} litre^{-1}) are converted to DMS derivatives of Pt(IV), but these products were not identified or determined. In a study by Boucher and Bosnich[21] a method is given for the preparation of the complex *cis*-$[Pt(DMSO)(C_2H_4)Cl_2]$ from $K[Pt(DMSO)Cl_3]$ and ethylene in aqueous HCl. It was noted in this case that an excess of acid leads to the reduction of DMSO catalysed

by platinum. However, in this article[21] as well, no details are given on the experiment.

Studies on the deoxygenation of inner-sphere sulphoxides have only recently started to be actively pursued. It was shown[22] that on dissolving the complex [Pt(II)(En)(DMSO)Cl]Cl (En = ethylenediamine) in a minimum solution for 2 days at 20 °C, deoxygenation of the sulphoxide ligand occurs and Pt(II) is oxidised to Pt(IV). The complex *cis*-[Pt(HEn)(DMSO)Cl_4]Cl is formed as a result. Fanizzi et al.[22] assumed that after opening of the ethylenediamine chelate ring and formation of $[Pt(HEn)(DMSO)Cl_2]^+$, the reaction takes place via a mechanism involving protonation of the inner-sphere DMSO molecule and a concerted redox conversion:



It has been established[23] that when the complex $H_2[Pt(DMSO)(\mu\text{-}O)Cl]_2$ (A) reacts with HCl in water with a molar ratio of (A) to HCl of 1:5, complex (A) is cleaved to form H[Pt(DMSO)Cl_3] and $[Pt(DMSO)(\mu\text{-}Cl)Cl]_2$. When the concentration of HCl is increased, these products are formed together with the sulphide complex *trans*-[Pt$(DMS)_2Cl_4$] (in 10–15% yield), the structure of which was established by X-ray diffraction analysis. Thus in this case also, a Pt(II) sulphoxide complex when treated with concentrated HCl is converted to a dimethyl sulphide derivatives of Pt(IV).

It was shown by Kukushkin et al.[24] that the deoxygenation of inner-sphere R_2SO molecules in platinum(II) complexes can have preparative importance. It transpired that the reaction between $(Et_4N)[Pt(II)(R_2SO)Cl_3]$ [R = Me, CH_2Ph(Bz), Ph] and HCl on heating the reaction mixture for several minutes in acetonitrile or nitromethane leads to the formation of the corresponding $(Et_4N)[Pt(IV)(R_2S)Cl_5]$ complexes, which were isolated in 80–90% yield. If HBr is used instead of HCl, the reduction of the sulphoxide and oxidation of Pt(II) is accompanied by replacement of the chloride ions in the complex by bromide ions. As a result of all these reactions, the compounds $(Et_4N)[Pt(R_2S)Br_5]$ were isolated.

It is important to note that the reaction of coordinated dibenzyl sulphoxide {in the complex $(Et_4N)[Pt(II)(Bz_2SO)Cl_3]$} with HCl takes place almost completely in favour of the deoxygenated ligand whereas reaction of free Bz_2SO with HCl is accompanied by rapid decomposition of the sulphoxide to form a mixture of products, amongst which PhCHO, BzCl, Bz_2S_2, Bz_2S, and $Bz_2S_2O_2$ have been detected.[10] Hence it follows that the reactivity of coordinated and free Bz_2SO towards HCl is substantially different. This result, so far the only one, suggests that the reduction of sulphoxides in complexes using HCl is promoted by the Pt(II) ion.

III. Conversion reactions of DMSO in systems of the type M–DMSO–RX

It was shown in a number of studies[25–35] that the reaction between the components of systems of the type M–DMSO–RX (R = H, Alk, X = Cl, Br, I) results in the deoxygenation of DMSO with the formation of DMS or secondary conversion products of DMS. The mechanism of these processes is quite complex (as is shown, for example, in four studies[31–34]). Nevertheless, it was found that an oxidisable metal promotes reaction between the components of the redox system. It may also be assumed that in the case of the reaction between metals and DMSO and HX, the resulting intermediate $Me_2\overset{+}{S}X$ is reduced by metals or metal ions formed at an intermediate stage of the process and which are oxidised and form complexes. Some of these complexes have been isolated and identified (Table 1).

IV. Reaction between inner-sphere DMSO in Pt(II) complexes and $SOCl_2$

The ability of thionyl chloride to deoxygenate free molecules of alkyl and aryl sulphoxides has been reported in the literature.[36–41] Usually these reactions take place with the formation of chloroalkyl or chloroaryl sulphides. In particular, it was established[36] that DMSO reacts with thionyl chloride at a molar ratio of 1:2 in dichloromethane to form $MeSCH_2Cl$, which was isolated in 92% yield. When diphenyl sulphoxide is reacted with $SOCl_2$, a mixture of diaryl sulphides — Ph_2S, $(p\text{-}ClC_6H_4)SPh$, and $(p\text{-}ClC_6H_4)_2S$ — is formed in the ratio 0.36:0.59:0.05 respectively.[38]

It was found[39] that coordinated DMSO reacts with $SOCl_2$ in a different way to when it is free. It transpired that the reaction of the complexes $(Et_4N)[Pt(DMSO)Cl_3]$ and *cis*-[Pt(DMSO)$(DMS)Cl_2$] with $SOCl_2$ at 20 °C in acetonitrile takes place for several minutes and gives DMS derivatives of Pt(IV) — $(Et_4N)[Pt(DMS)Cl_5]$ and *cis*-[Pt$(DMS)_2Cl_4$]. The reaction between the bis-sulphoxide complex *cis*-[Pt$(DMSO)_2Cl_2$] and $SOCl_2$ is interesting:

$$cis\text{-}[Pt(DMSO)_2Cl_2] + SOCl_2 \rightarrow cis\text{-}[Pt(DMS)(DMSO)Cl_4] + SO_2.$$

In this process only one coordinated DMSO molecule is reduced.

Thus the reaction of Pt(II) DMSO complexes with $SOCl_2$ results in the deoxygenation of DMSO and the oxidation of Pt(II) to Pt(IV); the formation of $MeSCH_2Cl$ during the reactions has not been observed. These reactions of coordinated sulphoxides have parallels in preparative organic chemistry. In particular, it was shown in three studies[39–41] that the formation of chlorinated disulphides can be avoided if the deoxygenation of R_2SO with thionyl chloride is carried out in the presence of cyclohexene[39] or sodium iodide.[41] Both of these compounds combine with chlorine. For example, the overall reaction of R_2SO with $SOCl_2$ in the presence of cyclohexene is represented by the equation

$$Ar_2SO + SOCl_2 + C_6H_{10} \rightarrow Ar_2S + SO_2 + C_6H_{10}Cl_2.$$

It may be assumed that in the reaction of Pt(II) sulphoxide complexes with $SOCl_2$, platinum(II) also acts as a chlorine-binding site. In this case Pt(IV) DMS complexes are formed.

The fact that in the reaction of the bis-sulphoxide complexes *cis*- and *trans*-[Pt$(DMSO)_2Cl_2$] with excess $SOCl_2$ only one of the DMSO ligands is reduced suggests that the processes involving reduction of DMSO and oxidation of Pt(II) are concerted.

Table 1. Initial reactants and conversion products in systems of the type metal–DMSO–RX.

Initial reactants	Products	Notes	Refs.
Pd–DMSO–n-$C_6H_{13}Br$	*trans*-[$Pd(DMS)_2Br_2$]		[25]
Rh–DMSO–n-$C_6H_{13}Br$	Rhodium(III) dimethyl sulphide complex	No information given on the structure of the rhodium and platinum complexes	[25]
Pt–DMSO–n-$C_6H_{13}Br$	Platinum(IV) dimethyl sulphide complex		
Au–DMSO–HBr	[(DMS)AuBr] and [$(DMS)AuBr_3$]	Both complexes were characterised by means of X-ray diffraction analysis	[26, 27]
M–DMSO–HX (M = Pd, Pt; X = Cl, Br)	*trans*-[$Pd(DMS)_2Cl_2$], [$Pt(DMS)_2Br_4$]	"	[28]
Noble metal–HX (X = Cl, Br)	Oxidation product of noble metal	No information given on the deoxygenation process	[29]
Ag–DMSO–HX (X = Br, I)	AgX, $(Me_3S)[AgX_2]$, $(Me_3S)[Ag_2X_3]$	$(Me_3S)[AgBr_2]$ complex was characterised by means of X-ray diffraction analysis	[30]
M–DMSO–CCl_4 (M = Fe, Co, Ni, Cu)	Metal oxidation products, DMS, CO_2, $COCl_2$, C_2Cl_6	Process takes place via the formation of dichlorocarbene	[31–34]

In concluding this section we should mention that the deoxygenation reactions of inner-sphere sulphoxides using $SOCl_2$ have parallels not only in organic but also organometallic chemistry. In particular, it has been shown[42–44] that acyl complexes can be deoxygenated with thionyl chloride or other acid halides to alkylidyne complexes

$$[M]—\overset{\overset{O}{\|}}{C}—R \rightarrow [M]\equiv C—R.$$

In these reactions also there is at least a formal reduction of the ligand and oxidation of the metal ion by the action of the acid chloride.

V. Deoxygenation of sulphoxides coordinated to Pt(II) with the reagent system PCl_5–ROH

It is known that in the reaction of phosphorus(V) pentachloride with different types of platinum(II) complexes, oxidative chlorination of the complexes occurs, giving platinum(IV) derivatives.[45–49] Fully in accordance with this are the reactions of the complexes K[$Pt(DMSO)Cl_3$] and [$Pt(R_2SO)LCl_2$] (R = Me, Et, $^1/_2C_2H_4OC_2H_4$, L = R_2SO; R = Me, L = DMS, NH_3, piperidine, pyridine, 2- and 4-methylpyridine) with PCl_5 in acetonitrile or nitromethane, resulting in the formation of the corresponding Pt(IV) compounds.[50,51]

In particular, by reacting the complex K[Pt(II)$(DMSO)Cl_3$] with PCl_5 in MeCN followed by decomposition of the excess PCl_5 with water or ethanol and addition of tetraethylammonium chloride to the mixture, (Et_4N)[Pt(IV)$(DMSO)Cl_5$] was obtained. The structure of this compound was confirmed by X-ray diffraction.[51] The reaction occurs differently if 2-propanol is used instead of water or ethanol. In this case as a result of all of the stages of the reaction, there is the formation of the DMS derivative (Et_4N)[Pt(IV)$(DMS)Cl_5$], whose structure has also been confirmed by X-ray diffraction analysis.

Similar reactions are typical for other Pt(II) sulphoxide derivatives, such as complexes of the type [Pt(II)$(R_2SO)LCl_2$]. The latter react with PCl_5 and with the reagent system PCl_5–ROH in different ways:

$$[Pt^{II}(R_2SO)LCl_2]—\begin{cases}\xrightarrow{PCl_5} [Pt^{IV}(R_2SO)LCl_4]\\ \xrightarrow{PCl_5/ROH} [Pt^{IV}(R_2S)LCl_4]\end{cases}$$

It should be mentioned in particular that on addition of EtOH or 2-PrOH to a mixture of [Pt(II)$(R_2SO)LCl_2$] and PCl_5, the dialkyl sulphide derivatives [Pt(IV)$(R_2S)LCl_4$] are formed in all cases. A mixture of K[$Pt(DMSO)Cl_3$] and PCl_5 reacts with alcohols in a different way. Thus, introduction of 2-propanol leads to the formation of the complex $[Pt(DMS)Cl_5]^-$, while introduction of ethanol gives a $[Pt(DMSO)Cl_5]^-$ complex. It follows from a comparison of the results obtained that in at least one case (in the reaction with K[$Pt(DMSO)Cl_3$] or with Pt[$R_2SO)LCl_2$], an inner-sphere rather than free molecule of R_2SO is deoxygenated.

It may be assumed that in the reaction of the complexes K[$Pt(DMSO)Cl_3$] and [$Pt(R_2SO)LCl_2$] with PCl_5, oxidation of the Pt(II) ion to Pt(IV) occurs and the intermediate (A) is formed:

$$\left[\begin{array}{c}O^+PCl_4\\ \|\\ Pt^{IV}—SMe_2\end{array}\right]$$
(A)

The subsequent addition of water leads to the hydrolysis of the sulphur-containing ligand with the formation of a Pt(IV) dialkyl sulphoxide complex, while when 2-propanol is introduced it is reduced and a Pt(IV) dialkyl sulphide derivative is formed.

It is known from the literature that the deoxygenation reactions of free R_2SO molecules using PCl_5 occur quite readily. However, there are significant differences in the form of reduction of inner-sphere and uncoordinated dialkyl sulphides. Thus, the reaction between free DMSO in PCl_5 occurs rapidly and leads to the formation of $MeSCH_2Cl$.[52,53] However, no complexes with such a

ligand were detected amongst the products from the reaction of coordinated DMSO with PCl_5.[50,51]

In the literature there are also examples of the conversion of R_2SO molecules to R_2S using PCl_5–reducing agent systems (where NaI [41] or 1-morpholino-1-cyclohexene [54] act as the reducing agent) as well as acid halide–alcohol–amine systems [where the acid halide is $SOCl_2$ and Cl(O)C–C(O)Cl].[6] In the latter case reaction of DMSO with the acid halide results in the formation of the salt $[Me\overset{+}{S}Cl]Cl^-$, which then reacts with an alcohol in the presence of NR_3 according to the scheme:[6]

$$[Me_2\overset{+}{S}Cl]\,Cl^- \xrightarrow[-NR_3\cdot HCl]{MeCH(OH)Me,\ NR_3} \rightarrow [Me_2\overset{+}{S}{-}OCHMe_2]Cl^- \xrightarrow[-NR_3\cdot HCl]{NR_3} Me_2S + Me_2CO.$$

In contrast to the reactions of free DMSO, the introduction of NR_3 is not required for the deoxygenation of inner-sphere DMSO.[39,50,51] This difference in the nature of the processes is likely to be due to the change in reactivity of the DMSO molecule as a result of coordination.

VI. Conversion of sulphoxides on treatment with metal ions in lower oxidation states

It is indicated in a review article[55] that Ti^{3+} compounds are mild and quite specific reducing agents as a result of titanium having a high affinity for oxygen. It is this factor that determines the reactivity of Ti^{3+} in reduction processes. Thus, $TiCl_3$ is an excellent reducing agent for nitro and nitroso compounds, aromatic and aliphatic *N*-oxides, and also azoxy compounds and oximes.[55] The ability of Ti^{3+} to extract an oxygen atom has also been extended to deoxygenation reactions of sulphoxides.[56,57]

It was shown[58] that the reaction of R_2SO with $TiCl_3$ can be used for the synthesis of R_2S. Different aryl and alkyl sulphides were obtained by this method. Reduction takes place for 2–4 h on boiling the reactants in a methanol–dichloromethane solvent mixture. The respective sulphides were isolated in 70–90% yield. Ho and Wong[58] assumed that the reaction takes place according to the following scheme:

$$R_2S{=}O + Ti^{3+} \longrightarrow R_2\overset{+}{S}{-}O{-}Ti^{\cdot\cdot\cdot}\ (Cl^-) \longrightarrow R_2S + Ti{=}O^{2+}.$$

The proposed synthetic method[58] was subsequently adapted for the deoxygenation of other sulphoxides.[59,60]

The reducing power of Ti^{2+} is known to be greater than that of Ti^{3+}.[55] It has also been established that Ti^{2+} salts do not exist in aqueous solution as they are oxidised by water. However, Ti^{2+} compounds can be successfully generated in non-aqueous media, for example, by the reduction of titanium(IV) tetrachloride with zinc dust. Ti^{2+} derivatives obtained by this method were used[61] for the reduction of R_2SO (R = Alk, Bz, Ph) to R_2S. The process was carried out in an ether–dichloromethane solvent mixture at 20 °C and was complete after not more than 1 min. In another study[62] when $TiCl_4$ was reacted with LiH in THF (with a 1 : 4 molar ratio of reactants), "low-valent titanium complexes" were obtained. On boiling alkyl or aryl sulphides with these compounds in THF for 10 h, the corresponding sulphides are formed. The prolonged time and relatively high temperature of the synthesis should be noted here.

The possibility of reducing sulphoxides with tin(II) chloride in the presence of HCl was first demonstrated in 1947.[64] This method was subsequently improved.[64] The reaction is carried out by boiling a solution of dialkyl sulphoxide and $SnCl_2.H_2O$ in methanol with added HCl for 2–3 h.

Tin(II) chloride has been used[65–67] for the reduction of coordinated DMSO. It was shown that the reaction of the complex *cis*-$[Pt(II)(DMSO)_2Cl_2]$ or a mixture of $K_2[Pt(II)Cl_4]$ and DMSO in hydrochloric acid with $SnCl_2.H_2O$ for 5–7 min with heating (70–90 °C) gives *cis*- and *trans*-$[Pt(IV)(DMS)_2Cl_4]$ respectively. Pt(IV) complexes with diethyl and dipropyl sulphide ligands were obtained in a similar manner. Kukushkin et al.[65–67] assume that the reactions for formation of $[Pt(R_2S)Cl_4]$ complexes can occur in both the inner and outer sphere of the coordination compounds.

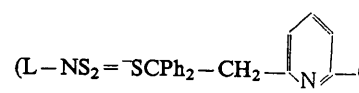
In concluding this section we should note that deoxygenation of sulphoxides can also be achieved using chromium,[68] vanadium,[69] molybdenum,[69,70] and tungsten[70,71] compounds in lower oxidation states.

VII. Reactions of sulphoxides with Mo(IV) complexes

The enzyme molybdenum oxotransferase is known to catalyse the two-electron oxidation or reduction of substrates of the type X/XO in a process which can formally be represented by the equation:

$$X + H_2O \rightleftarrows XO + 2H^+ + 2e.$$

It was demonstrated in a number of studies by Hold et al.[72–78] that $MoO(L{-}NS_2)(DMF)$ and $MoO_2(L{-}NS_2)$ complexes



($L{-}NS_2 = {}^-SCPh_2{-}CH_2{-}$ pyridine $-CH_2{-}CPh_2S^-$) are convenient

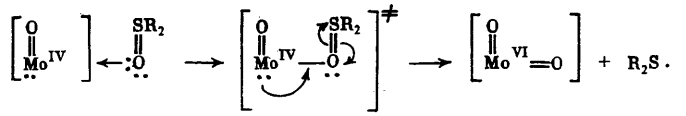
model compounds for the study of biological oxygen transfer processes. In particular, it was shown[74] that the compound $MoO(L{-}NS_2)(DMF)$ can effectively deoxygenate different alkyl and aryl sulphoxides. The process occurs in two stages. At the first stage the inner-sphere DMF is replaced by an R_2SO molecule:†

$$MoO(L{-}NS_2)(DMF) + R_2SO \rightleftarrows MoO(L{-}NS_2)(O\text{-}R_2SO) + DMF,$$

and deoxygenation takes place at the second stage:

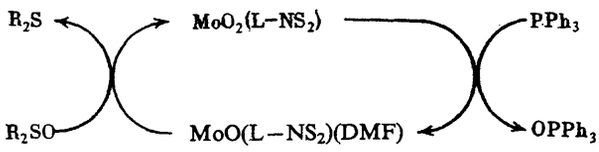
$$MoO\,(L{-}NS_2)\,(O\text{-}R_2SO) \rightarrow MoO_2\,(L{-}NS_2) + R_2S.$$

On the basis of the studies carried out,[74–78] the following reaction scheme was put forward:



† Inner-sphere *O*-coordinated sulphoxides will here and subsequently be denoted as *O*-R_2SO, while *S*-coordinated sulphoxides will be indicated as *S*-R_2SO.

It was shown in one of these studies[74] that the dioxomolybdenum complex $MoO_2(L-NS_2)$ oxidises triphenylphosphine to triphenylphosphine oxide. The following catalytic cycle was also established



It was shown in a number of studies[79–88] that certain other Mo(IV) complexes can effectively deoxygenate dialkyl sulphoxide molecules to give the corresponding sulphides. However, these processes have not been studied in detail.

VIII. Processes involving metal ion–reducing agent systems

In the previous section we considered deoxygenation reactions of sulphoxides using metal ions in low oxidation states that act simultaneously as electrophilic activators and reducing agents. However, metal ions in relatively high oxidation states can be used to deoxygenate R_2SO, but in this case chlorinated products are formed. Thus, in a study of the reactions of DMSO with $NbQX_4$ compounds (Q = X = Cl; Q = X = Br; Q = Me, X = Cl), XCH_2SMe products were obtained in all cases.[89–92] The authors of all four studies conclude that the process consists of two stages. At the first stage oxygen is transferred to give an oxocomplex and sulphonium salt:

$$NbQX_4 + 3Me_2SO \rightarrow NbOQX_2 \cdot 2Me_2SO + [Me_2\overset{+}{S}X]\,X^-,$$

At the second stage the sulphonium salt is converted to a haloalkyl sulphide:

$$[Me_2\overset{+}{S}X]\,X^- \rightarrow XCH_2SMe + HX.$$

The formation of XCH_2SMe can be avoided if the deoxygenation process is carried out using systems of the metal ion–reducing agent type. Complex hydrides of boron and aluminium are most frequently used as reducing agents.[93] This type of reduction of sulphoxides was first carried out in 1971.[94] In accordance with the recommended procedure stated in two studies,[94,95] the reduction was carried out by adding $NaBH_4$ slowly to a solution of R_2SO and $CoCl_2.6H_2O$ in 95% ethanol. Water was then added, heating was applied briefly, and the sulphides were extracted with ether. After removal of the ether the corresponding sulphides R_2S were isolated in good yield. The reduction of sulphoxides was also carried out using mixtures of $TiCl_4-NaBH_4$,[96,97] $TiCl_4-LiAl_4$,[98] $FeCl_3-NaBH_4$,[99] and Fe(III)LCl–$NaBH_4$ (L = tetraphenylporphyrinate).[100] The authors of all these studies[94–100] naturally assume that the process includes a stage involving *O*-coordination of R_2SO with the metal ion, resulting in electrophilic activation of the sulphoxide ligand and the sulphur atom becomes more sensitive to nucleophilic attack by hydride. It is important to note that the proposed mechanism has parallels in organic chemistry. In particular, reductions of alkoxysulphonium salts with complex boron hydrides have been reported.[101,102] An experiment carried out by Johnson and Phillips[102] demonstrated that the following conversion route occurs:

$$Ph-\overset{+}{S}(OMe)-Me \xrightarrow{[BH_4]^-} Ph-\overset{+}{S}(H)-Me \xrightarrow{-H^+} Ph-S-Me.$$

The reduction of sulphoxides with the reagent systems $BF_3.OEt_2-NaI$,[103] BF_3-NaI,[104] and $B(OPh)_3-NaBH_4$ [105] takes place via the same route.

In concluding this section we should report the results of one study[106] in which the conversions of dibutyl, dibenzyl, and diphenyl sulphoxides to the sulphides using aluminium(III) iodide in acetonitrile are recorded. It would appear that in these reactions the aluminium ion functions as the electrophilic activator and the I^- ions reduce the coordinated sulphoxides.

IX. Reduction of sulphoxides with carbonyl or carbene ligands in complexes

It is well known that the reactivity of carbon monoxide changes significantly when it is coordinated.[19] In a number of cases nucleophilic oxidation processes are made possible as a result of the electrophilic activation of CO molecules. According to studies that have been conducted, the mechanism of these types of reactions can be represented by the following scheme:

$$[M-CO] + \overline{O}-\overset{+}{A} \rightarrow \left\{M-C(=O)-O-\overset{+}{A}\right\} \xrightarrow{-CO_2} [MA].$$

Amine oxides, nitro- and nitroso-arenes, and iodosobenzene[107–109] have been widely used as oxygen donors in order to carry out these processes. It has been reported in a review article[108] that dialkyl sulphoxides can also act as this type of organic donor.

The reduction of sulphoxides by carbonyl complexes was first reported by Alper and Keung.[110] It was established that the reaction of various sulphoxides with $Fe(CO)_5$ at 130–135 °C in diglyme or di-n-butyl ether leads to the deoxygenation of R_2SO with the formation of the corresponding R_2S compounds and oxidation of an inner-sphere molecule of CO to CO_2. The nucleophilic oxygenation of the carbonyl ligand in the complex $[CpFe(CO)_3](PF_6)$ by DMSO and trimethylamine oxide has been studied.[111] Unfortunately, no information was given about the reduction products of dimethyl sulphoxide.[111]

It has been shown[112,113] that molybdenum hexacarbonyl is quite an effective agent for the deoxygenation of alkyl and aryl sulphoxides. The complex $Mo(CO)_6$ reduces sulphoxides on heating in solutions of dimethoxyethane[112] or acetic acid.[113]

Judging by the frequencies of the ν(CO) stretching vibrations in platinum(II) complexes, a CO ligand has high electrophilic activity.[107,108] The synthesis of the complex *cis*-$[Pt(DMSO)(CO)Cl_2]$ [ν(CO) = 2138 cm^{-1}] has been reported.[114] It has also been shown that heating this compound gives a mixture of products, amongst which CO_2 and CH_3Cl were identified. In the IR spectra of the solid products of thermolysis, the absorption bands characteristic of inner-sphere DMSO had disappeared. Pakhomova et al.[114] regard these results as an indication of the redox nature of the interaction between the coordination DMSO and CO ligands.

Deoxygenation of R_2SO molecules also occurs in processes involving another platinum(II) carbonyl compound—the complex $(Ph_3PBz)[Pt(CO)Cl_3]$ [ν(CO) = 2081 cm^{-1}]. Thus it was shown[115] that reaction of this complex with sulphoxides R_2SO (R = Me, Et,

n-Pr, Bz) in a nitromethane–acetic acid solvent mixture for several hours leads to the formation of $(Ph_3PBz)[Pt(R_2SO)Cl_3]$. On maintaining the complex $(Ph_3PBz)[Pt(CO)Cl_3]$ and the respective sulphoxide in an atmosphere of CO (1 atm, 20 °C, 5–7 days) in $MeNO_2$–$MeCO_2H$, deoxygenation of R_2SO molecules occurs and sulphides R_2S are formed. The reduction of sulphoxides by carbon monoxide does not occur in the absence of $(Ph_3PBz)[Pt(CO)Cl_3]$.

It was also shown in the same study[115] that reaction of $(Ph_3PBz)[Pt(R_2SO)Cl_3]$ complexes with CO under the conditions described above gives R_2S and $(Ph_3PBz)[Pt(CO)Cl_3]$ as the main products of synthesis. The reaction of $(Ph_3PBz)[Pt(Ph_2SO)Cl_3]$ with CO gives Ph_2S and a mixture of unidentified platinum-containing products. Preliminary results[115] suggest that the deoxygenation of R_2SO using CO in the presence of $(Ph_3PBz)[Pt(CO)Cl_3]$ is catalytic in nature.

The carbon atom that is bound to the central atom in carbene complexes is known to be activated as an electrophile. In the same way as for metal carbonyls, nucleophilic oxygenation reactions are typical for such compounds. Fairly recently Fisher et al.[116] obtained results indicating that DMSO can be deoxygenated by $(OC)_5W[C(R)Ph]$ complexes (R = H, Ph, OMe]. As a result of a redox reaction, the tungsten DMS complex $(OC)_5W(SMe_2)$ and O=C(R)Ph are formed.

X. Processes that occur in sulphoxide phosphine complexes

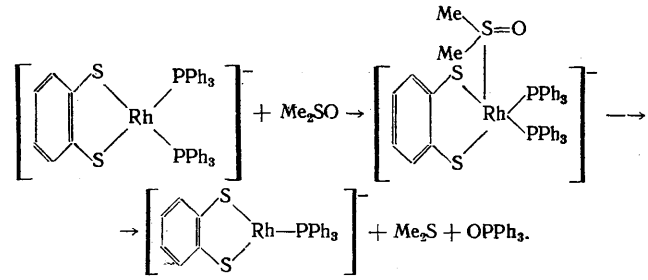
Bryan et al.[117] have reported the deoxygenation of DMSO that occurs to the following equation

$$[ReO(PPh_3)_2Cl_3] + 2Me_2SO \xrightarrow[C_6H_6]{HCl} \rightarrow [ReO(Me_2S)(OPPh_3)Cl_3] + Me_2S + OPPh_3.$$

The synthesis of $[ReO(Me_2S)(OPPh_3)Cl_3]$ takes place in the presence of hydrogen chloride, which is itself a reagent capable of deoxygenating DMSO. However, the process can also occur in the absence of HCl, but in this case the yield of DMS complex is reduced slightly (75% instead of 95%). It was also noted that $[ReO(Me_2S)(OPPh_3)Cl_3]$ is not formed when $[ReO(PPh_3)_2Cl_3]$ is treated with DMS or $OPPh_3$. It is thought[117] that the reaction mechanism includes a stage involving *O*-coordination of the DMSO molecule. The metal ion in this case functions as an electrophile activator, increasing the partial positive charge on sulphur and weakening the S–O bond. Subsequently there is a reaction with triphenylphosphine, which deoxygenates the DMSO molecule. It should be mentioned in connection with this study[117] that a process similar to that described in it had previously been reported.[118] It was established[117,118] that HCl catalyses the deoxygenation of DMSO by triphenylphosphine. This process also includes a stage involving electrophilic activation of DMSO by protonation of sulphinic oxygen.

On keeping $[M(Dppe)(O\text{-}DMSO)Cl]ClO_4$ complexes [M = Pt, Pd; Dppe = 1,2-bis(diphenylphosphino)ethane] in a mixture of dichloromethane and DMSO for a month (M = Pt) or 3 h (M = Pd), DMSO is deoxygenated to give the DMS derivatives $[M(Dppe)(DMS)Cl]ClO_4$. The latter are unstable and dimerise, giving $[\{M(Dppe)Cl\}_2](ClO_4)_2$ and DMS.[119] Unfortunately, Davies et al.[119] give no information about the oxidation product or about the presence of phosphine oxide in the mixture after completion of the reaction.

The rhodium(I) complex—$(Me_4N)[Rh(PPh_3)_2(S_2C_6H_4)]$—reacts with DMSO in DMF-d_6 and catalyses the transfer of oxygen from DMSO to triphenylphosphine.[120] Sellman et al.[120] propose that the reaction scheme includes a stage involving coordination of DMSO with the rhodium(I) ion, activation of the ligand, and formation of DMS, triphenylphosphine oxide and a tricoordinate Rh complex stabilised by the solvent:

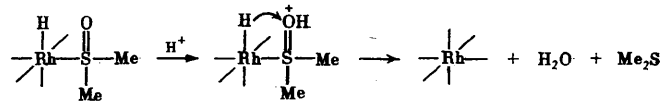


It should be noted that the conclusion, unsupported by experimental evidence, about *S*-coordination of the sulphoxide to the Rh(I) ion bound to other "mild" ligands raises certain doubts. As a rule in this situation DMSO is coordinated by its oxygen atom rather than by sulphur.[16–19] If our assumption is subsequently proved right, it may be possible to indicate more definitely that there is a similarity between the processes described in the three studies.[117,119,120]

XI. Other deoxygenation reactions of sulphoxides

The reduction of inner-sphere DMSO can occur when thermolysis of complex compounds in the solid state is carried out. Thus, it has been reported[121] that heating of the complexes $[Os(S\text{-}DMSO)_4Cl_2]$ and $[Os(S\text{-}DMSO)_3(O\text{-}DMSO)Cl_2]$ at 150 °C causes the disproportionation of dimethyl sulphoxide to give dimethyl sulphone and the complexes $[Os_2(\mu\text{-}SMe)_2(Me_2S)_2Cl_4]$ and $[Os(\mu\text{-}SMe)_2(Me_2S)(O\text{-}Me_2SO)Cl_4]$ respectively. The thermolysis of zirconium and hafnium compounds of the type $MCl_4.9DMSO$ has been described.[122] It was shown that heating these compounds in the solid state results in the formation of the hydroxo complexes $[M(OH)_2Cl_2(DMSO)_2]$ at an initial stage through a reaction with atmospheric moisture. When the temperature is increased further, conversion of the DMSO molecules occurs. Me_2S, HCl, and $Me_3S^+Cl^-$ were identified amongst the reaction products. Arsenin et al.[122] believe that the formation of DMS occurs in the inner sphere with the participation of HCl.

The deoxygenation of dialkyl sulphoxides using rhodium complexes was reported as early as 1969.[123] Thus it was shown that DMSO in the presence of $RhCl_3.3H_2O$ or *cis*-$[Rh(Et_2S)_3Cl_3]$ can be reduced with H_2 under mild conditions. By studying the kinetics of these reactions, it was possible to deduce that reaction of the initial compounds, DMSO and H_2 leads to the formation of sulphoxide hydride derivatives:



The subsequent reaction route involves protonation of the sulphinyl oxygen atom of the ligand followed by elimination of water molecules and DMS from the inner sphere of the complex.

XII. Conclusion

It is well known that sulphoxides exhibit weak oxidising properties. For example, in water (pH 7) the redox potential of the Me_2SO/Me_2S pair is only 0.16 V [124]

$$Me_2SO + 2H^+ + 2e \rightleftarrows Me_2S + H_2O.$$

However, the reactivity of R_2SO molecules when coordinated changes significantly.

An analysis of data on the deoxygenation of sulphoxides with complexes and metal ions shows that in the vast majority of cases the first stage of the reaction consists of *O*-coordination of R_2SO molecules with an M^+ ion:

$$R_2SO + M^+ \rightarrow [R_2S{=}OM^+ \longleftrightarrow R_2\overset{+}{S}{-}OM].$$

Here the metal ion functions as an electrophilic activator which increases the partial positive charge on sulphur and makes the ligand more sensitive towards reaction with a reducing agent. In fact, analysis of a number of X-ray diffraction studies (for example, those of Cotton[125] and Elding[126]) demonstrates that there is a significant elongation of the S—O bond in complexes with *O*-coordinated R_2SO molecules in comparison with free molecules. This in turn suggests that there is a significant contribution of the structure $R_2\overset{+}{S}-OM$ in the mesomeric hybrid of the molecule. It should be noted here that electron-acceptor substituents R on the sulphur atom also assist this type of electrophilic activation.

When *S*-coordination of R_2SO molecules occurs, the contribution of a bipolar structure to the mesomeric hybrid of the molecule decreases.

$$\begin{array}{ccc} :\ddot{O}:^- & & :O: \\ | & & \| \\ Me_2S^+ : \rightarrow [M] & \longleftrightarrow & Me_2\ddot{S} : \rightarrow [M]. \end{array}$$

This is suggested by the X-ray diffraction data on S—O bond lengths for free and *S*-bonded R_2SO molecules (see, for example, the study of Davies).[7] This all signifies that the susceptibility of the oxygen atom of the inner-sphere R_2SO molecule to electrophilic attack will decrease. However, if acylation nevertheless occurs (particularly when active reagents such as PCl_5 or $SOCl_2$ are used), the coordinated sulphoxide becomes "doubly activated"—by the acyl residue on the oxygen atom and the metal ion on the sulphur atom. This type of species should evidently have a higher oxidising potential than an R_2SO molecule that is merely *O*-bonded. This may possibly account for the ease of the deoxygenation reaction of *S*-coordinated sulphoxides on treatment with hydrogen halides.

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Activation of the C–H bond by metal complexes

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ABSTRACT. Reactions involving the cleavage of C–H bonds by metal complexes in saturated and aromatic hydrocarbons and also in other compounds are examined. Some of these processes occur with formation of a carbon–metal bond, whilst in others the interaction of the complexes with the hydrocarbon takes place without direct contact between the metal atom and the C–H bonds. Metal compounds are widely used as initiators of the liquid-phase oxidation of hydrocarbons at relatively low temperatures. There is a prospect of creating new technologies for the chemical processing of petroleum and gas hydrocarbons, whereby they can be converted into valuable products, for example, into alcohols, ketones, and carboxylic acids, on the basis of processes involving metal complexes. The study of the metal complex activation of the C–H bond also makes it possible to understand and model the metalloenzyme-catalysed hydrocarbon oxidation reactions in the living cell.

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Contents

I.	Introduction	853
II.	Activation of hydrocarbons via the oxidative addition mechanism	855
III.	Reactions of hydrocarbons with high-valence metal compounds	857
IV.	Oxidation of saturated and aromatic alkyl-substituted hydrocarbons by oxygen	858
V.	Biological oxidation and its chemical models	859
VI.	Conclusion	861

I. Introduction

The catalytic reactions occuring with cleavage of the C–H bond in hydrocarbons and other compounds on treatment with metal complexes[1] constitute an extensive and important field of metal complex catalysis.[2] The problem of the activation of the C–H bond in fully saturated hydrocarbons (alkanes) which contain no π- or *n*-electrons and are therefore inert to many reagents which are usual in organic chemistry, is of special interest. Many fundamentally new stoichiometric reactions of alkanes (and arenes) with metal complexes (usually in a low oxidation state) were discovered in recent years, but to this day there is an acute need to seek procedures for the metal-complex catalysed introduction of functional groups into these hydrocarbons, i.e. for replacing hydrogen atoms by hydroxy-, carbonyl-, amino-, and other groups and also for obtaining alkenes and halogeno-derivatives from alkanes.

Bearing in mind the process mechanism, all the C–H bond activation reactions can be subdivided into three groups. Processes where organometallic derivatives, i. e. compounds containing an M–C σ-bond (M = transition metal), are formed as an intermediate or as the final product can be conveniently assigned to the *first group*.[3] The σ-ligand in the resulting compound is an organyl group (alkyl, aryl, vinyl, ethynyl, acyl, etc.). Subsequently the M–C σ-bond may be ruptured; naturally, in catalytic processes the dissociation of this bond is obligatory. The cleavage of the C–H bond with direct participation of a transition metal ion proceeds via the oxidative addition (OA) mechanism:

$$RH + M \rightarrow R—M—H$$

or an electrophilic substitution:

$$RH + M^{(n+)} \rightarrow R—M^{(n+)} + H^+.$$

In the case of electrophilic metallation of the aromatic nucleus, the reaction proceeds in two stages, the electrophilic species adding to the arene in the first stage with formation of a Wheland intermediate. The intermediate formed in the interaction of a saturated hydrocarbon with an electrophile is much less stable. It is therefore not surprising that the reactivities of alkanes and arenes in electrophilic substitution reactions are not the same (the reactivity of the latter is much higher). At the same time, the mechanism of the interaction of both saturated and aromatic hydrocarbons with complexes of metals in a low oxidation state is in principle the same (oxidative addition). The reactivities of arenes and alkanes in oxidative addition reactions with respect to metal complexes therefore usually differ insignificantly. Furthermore, the C–H bond in alkenes is cleaved via the same mechanism. Thus the first group includes reactions involving "true" metal complex activation of the C–H bond if such activation is understood as a process as a result or in the course of which the activated molecule is cleaved at the C–H bond and enters in the form of an organyl σ-ligand into the coordination sphere of the metal complex. The formation of weak inner- or outer-sphere adducts of alkanes with metal complexes or of π-complexes of aromatic and other unsaturated molecules with metal-containing fragments need not by any means necessarily lead to the subsequent cleavage of the C–H bond; such coordination may be referred to as preactivation of the C–H bond of the compound.

In the *second group*, it is useful to include reactions in which the C–H bond is cleaved on treatment with a metal complex but the C–M σ-bond is not generated directly at any stage. The function of the metal complex usually consists under these conditions in abstracting an electron or an H atom from the RH molecule. The radical-ions RH^+ or radicals $R^\cdot$ formed then interact with other

species present in solution, for example, with molecular oxygen. One of the ligands of the metal complex can also serve as a species of this kind. An example is provided by the hydroxylation of an alkane by an oxo-complex of a high-valence metal:

$$RH + O{=}M^{(n+)} \rightarrow R^{\cdot} + HO{-}M^{((n-1)+)} \rightarrow ROH + M^{((n-2)+)}.$$

Here the oxo-complex is an oxidant of the type CrO_4^{2-} or MNO_4^- and also, for example, one of the states of the cytochrome P-450 enzyme (an oxoferryl species containing the $P^+.Fe^V = O$ species). It is noteworthy that the reaction with the intermediate participation of radicals can result in the formation of alkyl σ-complexes {for example, via the mechanism $RH + M^{(n+)} \rightarrow R^{\cdot} + M^{((n-1)+)} + H^+ \rightarrow R{-}M^{(n+)} + H^+$} and the reaction should then be assigned to the first group. Since the alkyl σ-derivative is frequently unstable, it is occasionally difficult to demonstrate its intermediate formation. The mediated (i.e. without contact with the metal ion) activation of RH by a complex can apparently be effected also via a molecular mechanism where RH is in direct contact only with a ligand of the complex. Finally the metal complex is capable of activating not only a hydrocarbon but also other reactants. Thus the active centre of cytochrome P-450 initially causes the transition of the oxygen molecule to a reactive state (one of the two atoms of dioxygen is coordinated to the iron ion, forming an oxo-ligand), after which it activates the hydrocarbon molecule.

Whereas the reactions included in the second group require direct contact between a molecule of the C–H compound and the metal complex (albeit via the ligand), in the processes belonging to the *third group* the complex activates initially not the hydrocarbon but the other reactant, for example, O_2 and H_2O_2, and the reactive species formed (a radical or carbene) rarely attacks the hydrocarbon molecule. In the H_2O_2–Fe(II) system, such a species is $HO^{\cdot}$. Sometimes the reaction initiated via this mechanism can lead to the formation of an organyl σ-derivative of the metal and the entire process then belongs to the first group. For example, the photochemical metallation of a C–H compound by a metal chloride can proceed in accordance with this scheme:

$$RH + [M{-}Cl]^* \rightarrow R^{\cdot} + M + H^+ + Cl^- \rightarrow \sigma\text{-}R{-}M + H^+ + Cl^-.$$

Evidently the unambiguous assignment of a process to a particular group requires a detailed knowledge of the reaction mechanism. However, at the present time the mechanisms of many processes have not been elucidated even in broad outline. We may note that the mechanisms of reactions included in the last two groups are in general not the same for paraffins, on the one hand, and aromatic hydrocarbons, on the other, although the products of these reactions can be frequently of the same type (for example, alcohols and phenols). Hence follows the possibility that arenes and alkanes may exhibit different reactivities in each specific reaction.

Although the H_2O_2–Fe(II) system, capable of hydroxylating aromatic compounds, was discovered as early as the past century,[4] the 1930s should apparently be regarded as the start of investigations into the activation of C–H compounds with participation of transition metal complexes. During this period, the reaction involving the electrophilic auration of arenes was discovered,[5] the radical chain autoxidation of hydrocarbons initiated by metal derivatives was developed,[6,7] and a method was proposed for the oxidation of alkenes and arenes by hydrogen peroxide in the presence of oxo-complexes.[8] The second spurt in the pioneering research into this field occurred in the 1960s. Reactions involving the cyclometallation (i.e. the cleavage of the C–H bond in a ligand linked to the metal via an atom of nitrogen, phosphorus, or another element) of the aromatic nucleus[9] and of an sp^3-hybridised carbon atom[10] were discovered. It was found that palladium(II) derivatives induce the oxidative coupling of arenes[11] and the arylation of alkenes,[12] while platinum(II) salts catalyse the H–D exchange with D_2O in benzene[13] and also in methane and other alkanes (a cobalt complex can also catalyse such processes).[14] It has now become evident that organometallic derivatives are formed as intermediates in all these instances. It was shown in the 1970s that alkanes are oxidised by platinum(IV),[15] palladium(II),[16] and ruthenium(IV)[17] compounds, that iridium(III)[18] and titanium(II)[19] complexes catalyse the H–D exchange, that Ziegler–Natta catalysts induce the hydrometallation of ethylene by methane with formation of propane,[20] and that the $PtCl_6^{2-}$ ion effects the electrophilic metallation of arenes.[21] The next decade was marked by a vigorous development of studies on the activation of alkanes (and arenes) by low-valence metal complexes via the oxidative addition mechanism with formation of alkyl σ-derivatives or alkenes.[22–27]

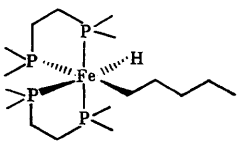
The number of known examples of the activation of the C–H bond by complexes of metals in a high oxidation state with formation of organometallic compounds is so far very small. Thus $PtCl_6^{2-}$ photochemically dehydrogenates alkanes and platinates arenes,[28] while the methyllutetium σ-complex enters into an exchange reaction with $^{13}CH_4$.[29] At the end of the 1980s, the intensity of investigations of the activation of the C–H bond by low-valence metal complexes began to diminish somewhat and interest gradually shifted to the field involving the oxidation of hydrocarbons by high-valence metal oxo-compounds and oxygen. Attention is being especially concentrated nowadays on biological oxidation and its chemical models. Studies on the modelling of cytochrome P-450 were stimulated by the use of iodosobenzene as the donor of an oxygen atom in catalytic oxidation reactions and of metalloporphyrin as a model of the active centre of the enzyme.[30] The Gif system, used for the selective oxidation of alkanes and consisting of O_2, an iron complex, a reductant, a carboxylic acid, and pyridine,[31] is of interest.

Studies on the activation of the C–H bond published up to 1987 were described in our previous review.[32] Therefore mainly publications during 1987–1990 will be discussed here. During this period, several books and reviews, wholly or partly devoted to the metal complex activation of C–H compounds, appeared.[2,33–51] We may also note that abstracts of the reports of the IInd All-Union Symposium on Homogeneous Catalysis "New Pathways in the Reactions of Saturated Hydrocarbons" have been published (Donetsk, 1988). All the papers in the special edition of the journal *Nouv. J. Chim.*, 1989, **13**, Nos. 10–11, are concerned with the activation of alkanes. The biological oxidation of hydrocarbons and the oxidation of hydrocarbons modelling the biological process (biomimetic oxidation) as well as the activation of oxygen have been described in abstracts published in a special issue of the journal *J. Inorg. Biochem.*, 1989, **36**, Nos. 3 and 4.

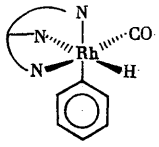
II. Activation of hydrocarbons via the oxidative addition mechanism

1. The formation of organyl σ-derivatives of metals

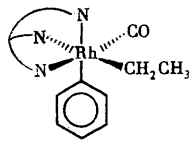
Numerous reactions involving the oxidative addition of the components of the C–H bond to metal complexes, in accordance with the scheme RH + $ML_n \rightarrow R-ML_n-H$ were discovered and investigated in detail in recent years. Alkanes, arenes, alkenes, and monosubstituted acetylenes enter into such reactions. The reaction frequently occurs in solution at room temperature, but sometimes heating is required. Certain reactions are stimulated by irradiation. An increased temperature or light are essential for the abstraction of several ligands from the initial complex and the formation of a coordinatively unsaturated species capable of effecting the oxidative addition of the C–H compound to itself. Thus irradiation at −90 °C of the phosphine complex $(PP)_2Fe(H)_2$, where PP = 1,2-bis-(dimethylphosphino)ethane, leads to the abstraction of a hydrogen molecule and the formation of the $Fe(PP)_2$ species. n-Pentane undergoes oxidative addition to this species with formation of the alkyl metal hydride complex (I).[52]



(I)

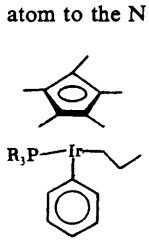


(II)

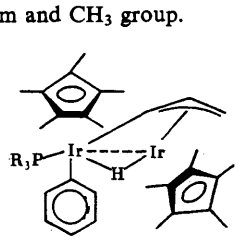


(III)

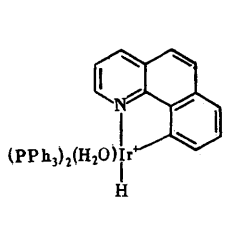
Sometimes thermal and photochemical activation can result in the formation of different products. For example, whereas heating of the solution of the ethylenerhodium carbonyl complex $[RhHBPz^*_3(CO)(C_2H_4)]$, where Pz* = 3,5-dimethylpyrazole, in benzene entails the elimination of the ethylene π-ligand and the formation of phenylrhodium hydride (II),[53] on irradiation of this solution, the hydride ligand adds not to the metal atom but to the ethylene molecule, which results in the appearance of an ethyl σ-group in the complex (III).[54] The hydrogen atom can add also to the allyl π-ligand: thermolysis of the complex $Cp^*Ir(H)(\eta^3\text{-}C_3H_5)$, where Cp* = pentamethylcyclopentadienyl, in benzene in the presence of phosphine leads to the formation of the propyl σ-derivative (IV).[55] It was of interest that at high concentrations of the initial complex the dimer (V) is obtained. It follows from the examples quoted that alkanes and arenes interact with metal complexes via the oxidative addition mechanism in a similar manner. However, differences are also sometimes observed. For example, the cyclometallation of 7,8-benzoquinoline by the complex $[LIr(PPh_3)_2]SbF_6$, where L = cycloocta-1,5-diene, in moist CH_2Cl_2 affords compound (VI),[56] whereas the analogous reaction with 8-methylquinoline does not entail the cleavage of the C–H bond in the methyl group and leads merely to the coordination of the Ir atom to the N atom and CH_3 group.



(IV)

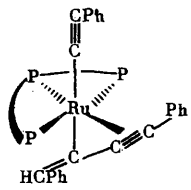


(V)

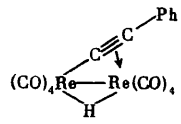


(VI)

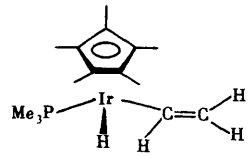
Complexes readily cleave the C–H bond in acetylenes and acetylene molecules frequently also enter into other reactions. Thus the interaction of $RuH_4(Cyttp)$, where Cyttyp = $PhP[(CH_2)_3P(C_6H_{11})_2]_2$, with an excess of phenylacetylene gives rise to compound (VII).[57] Irradiation of a solution of phenylacetylene and $Re_2(CO)_{10}$ in ether leads to the dinuclear rhenium hydride derivative (VIII).[58]



(VII)



(VIII)



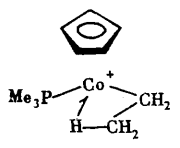
(IX)

Relatively few examples of the oxidative addition of ethylenes to the C–H bond are known. The thermolysis of the cyclohexyliridium hydride complex $Cp^*Ir(PMe_3)(H)(C_6H_{11})$ in solution in cyclohexane in the presence of ethylene results in the formation of the products of insertion in the C–H bond (IX) and of the ethylene π-complex $Cp^*Ir(PMe_3)(C_2H_4)$.[59] Finally, the components of the C–H bond in the allyl position are also capable of the oxidative addition to metal complexes: irradiation of a solution of the propene π-derivative $Cp^*Re(CO)(CH_2CHCH_3)$ affords the η^3-allylrhenium hydride complex $Cp^*Re(CO)(H).(\eta^3\text{-}CH_2CHCH_2)$.[60]

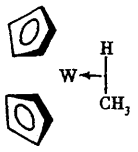
2. The reaction mechanism

The cleavage of the C–H bond can be preceded by the coordination of the saturated compound or fragment to the metal complex. Numerous complexes with hydrogen molecules have become known in recent years[61–64] and intramolecular coordination of the hydrogen atom of the C–H bond to the metal atom of the complex has been observed (the agostic C–H→M bond).[61,65] Such a bond occurs, for example, in complex (X).[66] The study of the kinetics of the reductive elimination of the CH_4 molecule from the complexes $Cp^*_2W(CH_3)H$ [67] or $Cp_2W(CH_3)H$ [68] led to the discovery of the intermediate formation of the methane "σ-complex" (XI). The existence of an analogous intermediate has been postulated in the reaction involving the elimination of CH_4 from the methylrhenium hydride derivative.[69] Presumably the alkane σ-complexes arise in the oxidative addition reaction, which leads to the formation of alkylmetal hydrides. In the photochemical reaction involving the cleavage of the Si–H bond by the $CpMn(CO)_3$ complex, which models such a process, the first stage may be the displacement of one of the CO ligands by the R_3Si-H ligand with formation of the structure (XII).[70] The adducts of alkanes with metal complexes formed at a low temperature can be detected by IR spectroscopy.[71] It has been established[72] that methane inhibits the reaction of butyllithium with butyl iodide. It has been suggested that this effect is due to the coordination of methane to the lithium alkyl in the reaction or prereaction complex. The interaction of the C–H bond with the metal complex can occur with mediation by the ligand. Thus the C–H...O=Re interaction in the oxorhenium complex has been demonstrated by X-ray diffraction.[73] The

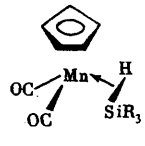
application of the NMR method led to the detection of the short-lived adducts of bis[hydrotris(pyrazolyl)borato]cobalt with alkanes in solution.[74] Outer-sphere interaction between the components takes place in this case.



(X)



(XI)



(XII)

The previous section presented examples of reactions which undoubtedly occur via the oxidative addition mechanism and in which the metal complex functions as a nucleophile. The kinetics and thermodynamics of such processes have now been investigated in fair detail[32,39,40,75,76] and quantum-chemical calculations have been carried out.[77,78] At the same time several reactions are known where attempts to describe their mechanisms as oxidative addition have encountered certain contradictions. In the first place, this applies to the activation, known for a long time, of alkanes by platinum(II) salts, which exhibit both nucleophilic and electrophilic properties. The activation of an alkane by a platinum(II) complex apparently begins as the oxidative addition of the C–H bond but the H atom acquires acid properties and is abstracted by a base (for example, the water forming part of the composition of the complex[79]):

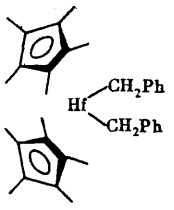
$$L_4Pt + RH \rightleftarrows [L_4Pt(H)R] \rightleftarrows L_3PtR + H^+ + L^-.$$

The rotation of the alkyl group R in the coordination sphere entails an appreciable intensification of the nucleophilic properties of the carbon atom, which should facilitate the electrophilic attack on the latter by the deuterium cation D^+:

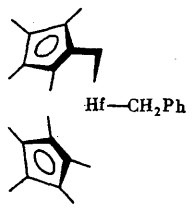
$$L_3PtCH_2R + D^+ \rightleftarrows L_3PtCHDR + H^+.$$

The alkyl group rotates synchronously with the approach of D^+ and the C–H→Pt agostic bond is formed. Since it is evident that several H atoms can be substituted by D in the alkyl group R before it is split off from Pt, the proposed mechanism explains satisfactorily the multiplicity of different types of H–D exchange in the presence of platinum(II) complexes.[79] It is believed[79] that such "alkyl" mechanisms agree better with certain features of the exchange reaction than the carbene and alkane–alkyl mechanisms proposed previously.[1,32,80]

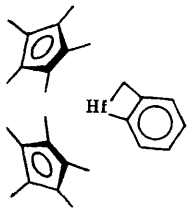
The intermolecular activation of the C–D bond in benzene-d_6 by the complex $(PMe_3)_2Pt(CH_2CMe_3)(SO_3CF_3)$ apparently begins with the formation of the coordinatively unsaturated species $[(PMe_3)_2Pt(CH_2CMe_3)]^+$, which gives rise to an arylplatinum hydride complex with C_6D_6 as a result of oxidative addition.[81] The product $(PMe_3)_2Pt(C_6D_5)(SO_3CF_3)$ is formed after the elimination of CH_2DCMe_3. However, Brainard et al.[81] do not rule out the possibility that the positively charged species carries out an electrophilic attack on the benzene ring. Thermolysis of complex (XIII) in benzene-d_6 leads to the appearance of the intramolecular metallation product (XV).[82] The reaction takes place in several stages and the intermediate complex (XIV) has been isolated. The introduction of several substituents into the benzene ring has virtually no effect on the rate of metallation, which enabled the authors[82] to regard the transformation (XIV)→(XV) not as typical electrophilic metallation by the Hf(IV) ion but as a process which proceeds via a four-membered transition state.



(XIII)



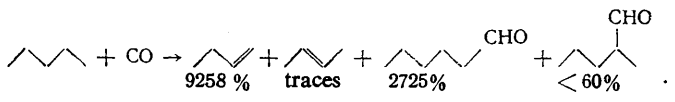
(XIV)



(XV)

3. Catalytic Processes

Metal complexes induce a whole series of reactions involving the substitution of hydrogen atoms in hydrocarbons by the atoms of other elements—processes involving the introduction of a functional group into the C–H bond. The complex very often catalyses such reactions. A considerable proportion of the processes proceed via the oxidative addition mechanism. Thus the complex $Li_2Pd_2Cl_6$ catalyses the H–D exchange in the allylic position in alkenes with CD_3COOD.[83] It has been suggested that the exchange proceeds with the reversible intermediate formation of an alkene π-complex of palladium(II) and its conversion into allylpalladium(IV) hydride π-derivative. The H–D exchange involving alkylsilanes catalysed by an osmium complex has been described.[84] Metal complexes dehydrogenate alkanes to alkenes. In a dark reaction, cyclohexene is formed from cyclohexane in the presence of $[PtCl_2(SnCl_3)_2]^{2-}$,[85] the complexes $[Ir(H)_2(\eta^2\text{-}O_2CCF_3)(PR_3)_2]$ dehydrogenate alkanes in the presence of 3,3-dimethylbutene, both on heating and on irradiation.[86] $RhCl(CO)(PMe_3)_2$ proved to be an effective photocatalyst of the dehydrogenation of alkanes.[87] Under the same conditions, arenes enter into an oxidative coupling reaction with alkenes, which results in the formation of substituted styrenes.[88] Finally, the above catalyst has been used for the photochemical introduction of functional groups into alkanes and arenes. Thus a complex mixture of products has been obtained from pentane and CO (the yields of the product relative to the catalyst are given below):[89]



It is of interest that the composition of the products depends on the wavelength. On irradiation of decane with light at a wavelength in the range $420 > \lambda > 295$ nm, the principal products are non-1-ene and undecanal. At $\lambda > 325$ nm, mainly isomeric C_{11} aldehydes are formed, while non-1-ene is not detected at all.[90] Irradiation with light of a solution of $RhCl(CO)(PBu_3)_2$ in pentane in the presence of cyclohexyl isocyanide leads to the formation of imines in low yields.[91] Finally, under the same conditions it is possible to silylate arenes with triethylsilane or hexamethyldisilane.[92] It is noteworthy that, on photosensitisation with mercury, dicyclohexane, cyclohexylmethanol, and ethylene glycol are formed from cyclohexane and methanol.[93]

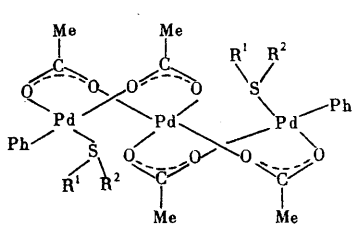
The kinetics of the hydromethylation of acetylene by methane have been investigated in the presence of organonickel catalysts.[94] The use of $^{13}CH_4$ in an analogous system made it possible to show that propene is formed via at least two pathways and that the contribution of the pathway involving methane is only about 20%.[95] At the same time, a detailed study of the hydromethylation of acetylene by methane in the presence of $Pt(bipy)Cl_2$ in dimethylformamide showed that the products of the reaction of a mixture of $^{13}CH_4$ and C_2H_2 do not contain ^{13}C and do not differ as regards composition and quantitative yield from the products of the reaction of pure C_2H_2.[95]

III. Reactions of hydrocarbons with compounds of high valence metals

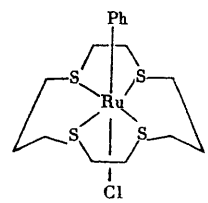
Whereas the interaction of C–H compounds with complexes of metals in a low oxidation state usually proceeds as oxidative addition, the reactions of arenes or alkanes with the derivatives of metals in high oxidation states are usually processes involving direct electrophilic substitution leading to the formation (final or intermediate) of an organometallic compound or are electron transfer or hydrogen atom abstraction processes, which are followed by the reactions of the resulting radical-cation or radical.

1. Direct electrophilic metallation of the C–H bond

In recent years electrophilic substitution by metal complexes of a hydrogen atom in aromatic compounds has been studied in detail in relation to cyclometallation reactions and in particular *ortho*-palladation (see, for example, Refs. 96–101). The reaction involving the intramolecular and intermolecular exchange of a cyclopalladated ligand in complexes has been discovered.[99–101] Previously such transfer of an aryl σ-ligand between complexes of the same metal had been observed for platinum(IV) derivatives[102] and also thallium(III) and mercury(II) derivatives. Palladocyclic compounds can be used to introduce functional groups into arenes.[103] It is well known that arylpalladium(II) σ-complexes, not stabilised by chelating ligands, are unstable and readily decompose with formation of biaryls (see, for example, Ignatenko et al.[104]). However, it has been recently possible to isolate the first phenylpalladium(II) σ-derivative, obtained directly by palladating benzene. When palladium(II) acetate was heated in benzene in the presence of dialkyl sulphides, complexes (XVI) were obtained.[105] A similar reaction has been discovered for ruthenium(II): the chloride complex with a thio-crown-ether in the presence of $Al_2(CH_3)_6$ gives rise to the phenyl derivative (XVII) on heating in benzene.[106]



(XVI)



(XVII)

The complexes formed by metallating arenes with the $PtCl_6^{2-}$ ion are sufficiently stable to be able to isolate them in a crystalline state (they can be stored for several months at room temperature), but prolonged heating of a solution of an arene and $PtCl_6^{2-}$ in $CF_3COOH-H_2O$ or CH_3COOH leads to the formation of biaryls and platinum(II) derivatives.[107] Metallation of arenes by heating with the $PtCl_6^{2-}$ ions can be achieved only in an acid medium. At the same time the rate of the light-induced reaction, occurring in acetic acid in the case of anisole with a quantum yield of 0.08 (λ = 365 nm), is independent of the acidity of the medium; the reaction can be carried out also in CH_2Cl_2.[108] Intermediate platinum(III) complexes apparently arise in the reaction.[109] The unstable arylplatinum(IV) σ-complexes, formed in the thermal reaction of arenes with $PtBr_6^{2-}$ in a $CF_3COOH-H_2O$ mixture, were not isolated, but biaryls were detected in the products.[110]

All the reactions described above, in which the formation of aryl σ-derivatives of metals was demonstrated, proceed as typical electrophilic substitution processes.[111] Nevertheless, their first stage can consist in electron transfer from the arene to the metal and the formation of an arene radical-cation, after which a Wheland intermediate is formed. However, the radical-cation may not recombine with the reduced metal ion, undergoing instead further reactions with participation of other species, for example, nucleophiles.[112–114] In this case, the arene or alkylarene is activated by the metal complex without the intermediate formation of an organometallic compound.

Metal complexes with strong electrophilic properties are capable of reacting with alkanes.[115–117] Thus, on heating a solution of CH_4 and $Pd(OOCMe)_2$ in CF_3COOH, metallic palladium and CH_3OOCCF_3 are formed in a yield greater than 60% relative to palladium(II).[116,117] It has been suggested that the product is formed when a solvent molecule attacks the methylpalladium(II) σ-complex arising as a result of electrophilic substitution. Under these conditions, arenes are activated much more readily: the trifluoroacetate group substitutes a hydrogen atom in the *p*-xylene ring more than 50 times faster than in the methyl group. It has been suggested[118] that the oxidation of alkanes by oxygen in aqueous solutions of mercury(II) salts under UV irradiation involves the intermediate formation [as a result of the electrophilic attack by Hg(II)* on RH] of alkylmercury compounds, but proof of this requires additional studies. The intermediate formation of alkylplatinum(IV) σ-complexes on photochemical dehydrogenation of n-hexane to the hexeneplatinum(II) π-complex has not been demonstrated either.[32] The possibility of the occurrence of such a process, with participation of a stage involving the β-elimination of hydrogen from the alkyl chain, has been confirmed in a study[119] where it was shown that the β-elimination from the ethylplatinum(IV) complex is the principal route to its decomposition.

2. Functionalisation on treatment with oxygen-containing complexes

Oxo-compounds of transition metals (in the first place chromium and manganese) are effective oxidants for C–H compounds.[120] Such derivatives are used in organic synthesis; for example, the $KMnO_4-NEt_3$ system oxidises the benzyl group to the ketone group with a satisfactory yield.[121] There exist also other oxo-complexes capable of oxygenating hydrocarbons: $[Ru^{VI}L_2(O)_2]^{2+}$ (L = 6,6′-dichlorobipyridyl) [122] and $[Os^{VI}(CN)_4(O)_2]^{2-}$.[123] The second complex activates the C–H bond on irradiation.

The oxidation of alkanes and of aromatic alkyl-substituted compounds by oxo-derivatives of chromium(VI) has been investigated on irradiation with light.[124–127] CH_3COOH, CH_3CN, and CH_2Cl_2 have been used as solvents; the products are alcohol

and carbonyl compounds. The reaction apparently begins with the abstraction of a hydrogen atom from the C–H bond of the oxo-complex by an excited species. On irradiation with light, the oxidation of alkanes and arenes by vanadium(5+) oxo-complexes in organic acids is greatly accelerated.

Transition metal,[128] for example palladium[129] and chromium,[130] peroxide compounds are capable of effecting the stoichiometric oxygenation of alkanes. Various chromium,[131–134] ruthenium,[135] and vanadium[136,137] complexes catalyse the oxidation of alkanes by peroxides. In many reactions of this kind, either metal peroxides are formed or the substrate is oxygenated by the oxo-compound, which is regenerated on interaction with ROOH. An alternative mechanism may be the formation of $HO^{\cdot}$ radicals when ROOH is acted upon by the complex. The hydroxylation of benzene by the H_2O_2–Fe(II) system takes place in this way.[138] Cyclohexane has been oxidised to cyclohexanol by molecular oxygen at room temperature in solution in aqueous dioxane.[139] The reaction was catalysed by the ruthenium(III) complex of ethylenediaminetetraacetic acid (EDTA). It has been suggested that a μ-peroxo-complex or an oxo-complex is formed in the first stage and then hydroxylates the alkane:

$$LRu^{III} + O_2 \rightleftarrows LRu^{IV}\,O \ldots O \ldots Ru^{IV}\,L \leftrightarrow 2LRu^{V} = O.$$

On irradiation under anaerobic conditions, alkanes dissolved in CH_3CN are converted by treatment with heteropolyacids into alkenes, dimers, *N*-alkylacetamides, alkylmethyl ketones, and also H_2.[140,141] The reaction begins with electron or H atom transfer from RH to a photoexcited polyoxometallate species. The resulting $R^{\cdot}$ radical is converted into an alkene or interacts with a solvent molecule. The reduced species derived from the oxo-compound is reoxidised by Pt(O), evolving H_2. The use of the ROOH–CCl_4 (or CBr_4) system in dark reactions catalysed by heteropolyacids induces the halogenation of the alkane, while in the interaction of alkanes with the ROOH–$C(NO_2)_4$ system nitroalkanes are formed.[142]

IV. Oxidation of saturated and aromatic alkyl-substituted hydrocarbons by oxygen

1. Initiation of the oxygenation process by metal complexes

It is well known that variable-valence metal compounds are capable of initiating in solution radical chain hydrocarbon oxidation processes.[1] Chain initiation occurs, for example in accordance with the scheme $M^{3+} + RH \rightarrow M^{2+} + R^{\cdot} + H^{+}$, after which $R^{\cdot}$ interacts rapidly with oxygen: $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$. Chain propagation takes place via the reaction $ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$. Complexes are usually active in the decomposition of the hydroperoxides formed (see, for example, Lauterbach et al.[143]). The participation of a metal ion in a low oxidation state in the reaction leads to chain branching. Thus, in the cobalt bromide catalysis of the oxidation of hydrocarbons,[144,145] which is of practical importance, the interaction of one $ROO^{\cdot}$ radical with Co(II) leads to the formation of three new radicals (Scheme 1):

Scheme 1

$$ROO^{\cdot} + Co\,(II) + H^{+} \rightarrow ROOH + Co\,(III)$$
$$\downarrow Co(II) \qquad Br^{-}\downarrow RH$$
$$RO^{\cdot} + Co\,(III) \quad R^{\cdot}$$
$$Br^{-}\downarrow RH \qquad \downarrow O_2$$
$$2ROO^{\cdot} \xleftarrow{O_2} 2R^{\cdot} \qquad ROO^{\cdot}$$

In this process, bromide ions catalyse the oxidation of RH by a cobalt(III) derivative via the reaction

$$Co\,(III) + Br^{-} \rightarrow Co\,(II) + Br^{\cdot};\quad Br^{\cdot} + RH \rightarrow Br^{-} + H^{+} + R^{\cdot}.$$

The oxidation process may not have a chain mechanism in relation to the $ROO^{\cdot}$ radicals, as shown for the oxidation of *p*-ethylnitrobenzene at 140 °C in the presence of $Mn(OOCCH_3)_2$.[146]

In the reactions mentioned above, the role of the metal complex (and also the role of the ligand, as in cobalt bromide catalysis) consists in chain initiation and propagation. However, the complex can only generate reactive species which subsequently enter into a non-chain process, which proceeds with dissociation of C–H bonds. Thus, on interaction with copper(I) and H^{+} ions, molecular oxygen gives rise to the $HO^{\cdot}$ radicals ($2Cu^{+} + O_2 + 2H^{+} \rightarrow 2Cu^{2+} + H_2O_2$; $Cu^{+} + H_2O_2 + H^{+} \rightarrow Cu^{2+} + HO^{\cdot} + H_2O$), which then hydroxylate benzene to hydroquinone. The resulting copper(II) may be reduced electrochemically.[147] The interaction of O_2 with the copper(I) complex $Py_4Cu_4Cl_4$ leads to the formation of the copper(II) oxo-complex $Py_3Cu_4Cl_4O_4$, which is capable of catalysing the oxidative coupling of 2,6-dimethylphenol.[148]

2. Photocatalytic liquid-phase oxygenation

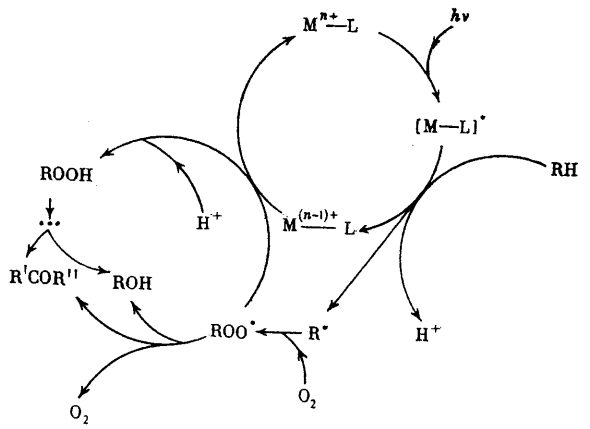
The metal complex-catalysed photochemical oxidation of hydrocarbons by air in solutions at room temperature is of great practical interest because it can serve as a basis for new processes for the conversion of hydrocarbon raw material using sunlight as the source of energy. We shall differentiate two principal groups of metal compounds capable of effectively catalysing the photooxygenation of alkanes: the halide complexes (usually chlorometallates) and the oxo-complexes (usually polyoxometallates).

The following systems for the photochemical oxidation of hydrocarbons have been discovered and(or) studied in detail in recent years: $FeCl_3$ in CH_3COOH [149,150] and in CH_3CN;[151,152] $CuCl_2$ in CH_3CN;[151,153] $AuCl_4^{-}$ in CH_3CN [154] and CH_3COOH;[155] $Cr_2O_7^{2-}$ and $Cr_4O_{13}^{2-}$ in CH_2Cl_2;[156,157] iso- and hetero-polyacids in H_2O,[158,159] CH_3CN,[160] CH_3COOH or CH_3OH,[161] and CH_2Cl_2;[162] vanadates in CH_2Cl_2;[162] UO_2^{2+} in CH_3COOH or CH_3CN.[163] The complexes $PtCl_6^{2-}$, $PtCl_4^{2-}$, $RuCl_3$, $RhCl_3$, $IrCl_6^{2-}$, and $OsCl_6^{2-}$ can also serve as photooxygenation catalysts in acetonitrile. Cyclohexane, isobutane, toluene, ethylbenzene, and other hydrocarbons are used as substrates. The methane oxidation reactions in the presence of polyoxotungstate in H_2O [158,189] or of $HAuCl_4^{-}$ [154] and UO_2Cl_2 [163] in CH_3CN afford formaldehyde (as well as methanol and formic acid). Irradiation of a solution of an alkane (adamantane, cyclohexane) in CH_3CN in the presence of cerium ammonium nitrate gives rise to alcohols and ketones.[164]

The proposed mechanism of the photochemical oxidation processes described, including the formation on treatment with the photoexcited metal complex species of the $R^{\cdot}$ radical (in the case of

oxo-complexes, an H atom from RH apparently adds to the oxygen ligand), is presented in Scheme 2.

Scheme 2



However, in fact the mechanism is apparently more complex, at least when halides are used. Thus the photooxygenation of alkanes catalysed by the complex $AuCl_4^-$ takes place with an induction period (which proved to be particularly long in the case of the bromides $CuBr_2$, $FeBr_3$, and $PtBr_6^{2-}$). The induction period becomes shorter after the introduction of an inductant into the solution. Presumably, the oxidation proceeds also via a second pathway in which the catalyst is a low-valence metal complex obtained from the initial complex during the initial period of the reaction. Thus the complex combines with an oxygen molecule and the metal peroxide derivative formed subsequently oxidises the hydrocarbon (one cannot rule out the possibility that this process takes place under the influence of light). Furthermore, the peroxide derivative can be converted into an oxo-complex of the metal in a higher oxidation state, which subsequently reacts with the alkane.

3. Coupled oxidation

A whole series of systems containing complexes are capable of effecting the oxidation of alkanes and arenes by oxygen only in the presence of a reductant. In this case, coupled oxidation takes place.[165] Detailed study of the oxidation of cyclohexane by atmospheric oxygen in the presence of hydrazobenzene (a reductant), benzoic acid, and the complex Py_4FeCl_2 (catalyst) in acetone led to the hypothesis that the reaction proceeds with the intermediate formation of an iron hydroperoxide derivative, which hydroxylates alkanes.[165] Hence it was concluded that, despite the participation of the iron complex, molecular oxygen, and the reductant in the process, the system cannot be regarded as a model of cytochrome P-450. At the same time the oxenoid species $Fe^V = O$, which is inserted in a C—H bond (X = OH, $OCOCH_3$), plays an active role in the oxidation of alkanes by the Gif system:

$$X_2Fe^{II} + {}^{\cdot}O_2H \rightarrow X_2Fe^{III}—O—O—H \xrightarrow{H^+,\ X^-} X_3Fe^V{=}O + H_2O.$$

Thus the authors of the study[167] in which evidence for the formation of such a species was secured believed that the Gif system can be regarded as a model of cytochrome P-450. However, there exists also an alternative idea about the nature of the Gif system,[168,169] according to which the active centre is a solvated oxygen cation PyO^+ formed via the reaction $HO_2^{\cdot} + PyH^+ \rightleftarrows PyO^+ + H_2O$. This radical-cation, capable of oxidising hydrocarbons, was generated electrochemically[168] and by the photochemical oxidation of pyridine *N*-oxide.[169]

V. Biological oxidation and its chemical models

Alkanes or arenes are surprisingly easily oxidised by atmospheric oxygen in cells of organisms at room temperature and the usual pressure. For example, various fungi hydroxylate camphor derivatives,[170] testosterone and other steroids,[171] and the side chain in alkylbenzenes.[172] Under the influence of the *Pseudomonas putida* bacteria, benzene has been converted into *cis*-1,2-dihydroxycyclohexa-3,5-diene.[173] The cells of higher animals and man are also capable of oxidising compounds containing C—H bonds, hydroxylation occurring with the invariable participation of a reductant, whereupon one of the two atoms in the O_2 molecule is inserted into the C—H bond, while the other is reduced to H_2O. This is referred to as the monoxygenase mechanism (the catalysis is effected by monoxygenase enzymes). In all the biological oxidation reactions, hydroxylation is preceded by the activation of oxygen by the metalloenzyme.[174] The creation of chemical models of the enzymic oxidation of alkanes and arenes makes it possible not only to understand better its mechanism but also to develop what are likely to be fundamentally new processes for the conversion of the hydrocarbon raw material.[175]

1. Cytochrome P-450

Cytochrome P-450 is a widely distributed enzyme in living nature; it belongs to the group of monoxygenases and is capable, in particular, of oxidising alkanes, arenes, and their derivatives (for example, prostaglandins and aliphatic acids).[176—178] The active centre of the enzyme incorporates haem iron (whose ion forms a complex with the porphyrin). On treatment with O_2 and a reductant, the $Fe^V = O$ fragment arises in the active centre and oxidises the alkane in accordance with the scheme

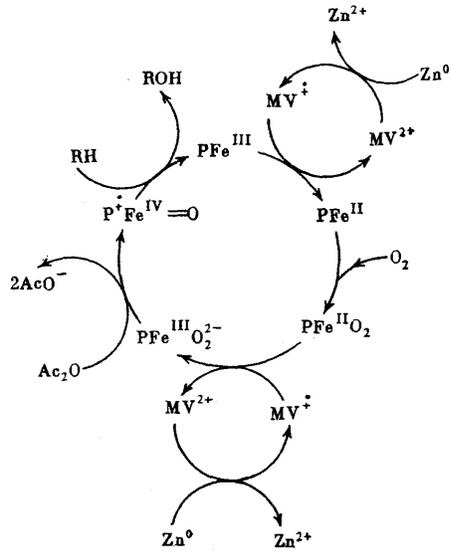
$$Fe^V{=}O + RH \rightarrow Fe^{IV}—OH + R^{\cdot} \rightarrow Fe^{III} + ROH.$$

The mechanism of the action of cytochrome P-450 has been described in detail in reviews[32,179] and other publications.[180,181]

In modelling cytochrome P-450 (see the reviews[32,175,179,182—184]), porphyrin complexes of iron(III) as well as manganese(III), chromium(III), and ruthenium(III) are usually employed as catalysts. If molecular oxygen is the oxidant, a reductant is required whose role may be assumed by an electric current.[185,186] Metallic zinc can also serve as the reductant.[187—189] The catalytic cycle involving the last system, which includes, apart from the porphyrin complex

PFe^{III}, an electron transferring agent (methylviologen MV^{2+}) and acetic anhydride, is illustrated in Scheme 3.[189]

Scheme 3

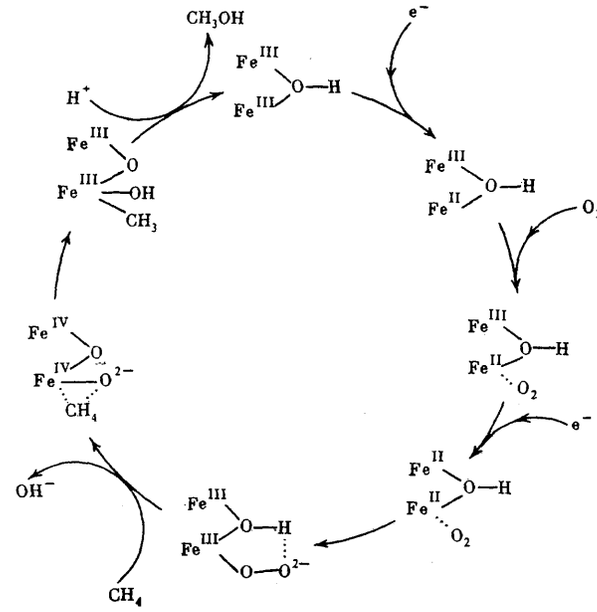


Instead of the O_2–reductant pair, one can employ oxo-compounds containing an oxygen atom which is already partly reduced: PhIO,[190] H_2O_2,[191–193] NaOCl,[194,195] $KHSO_5$,[196] and XeO_3.[197] We may note that, in the oxidation of alkanes in the presence of cytochrome P-450 or its models, the kinetic isotope effect reaches high values—up to 21.9 for the oxidation of cyclohexane by the tetramesitylporphyriniron chloride–NaOCl system.[198] For the oxygenation of hydrocarbons by various oxygen atom donors, fairly simple complexes were used as catalysts in certain studies: CrO_3 or $VOCl_2$ in the presence of α-picolinic acid (oxidation by PhIO),[199,200] $Fe(ClO_4)_2$ (oxidation by peroxybenzoates),[201] $[Fe(MeCN)_4](ClO_4)_2$ (oxidation by H_2O_2),[202] and $RuCl_2L_2$ (oxidation by LiOCl).[203]

2. Methane monoxygenase

Among the monoxygenases containing non-haem iron (the ligands are apparently aminoacid residues), methane monoxygenase (MMO) is of special interest. It catalyses the oxidation of alkanes, methane showing the highest activity among them in this reaction.[1,32] Ethane is also readily oxygenated by this enzyme.[204] It has been shown that MMO from *Methylococcus capsulatus* contains 4 atoms of non-haem iron and 1 atom of Cu per molecule with a molecular weight of 240 000.[205] The active centre of MMO apparently contains a dinuclear iron complex.[206] The proposed mechanism of the oxygenation of methane at this dinuclear centre is illustrated in Scheme 4.[207]

Scheme 4



Several systems which can serve as models of MMO in the oxidation of alkanes according to the authors have been described: the system incorporating a dinuclear μ-oxo-complex of iron, O_2, CH_3COOH, and Zn;[208] the cluster $Mn_{3-4}O_{1-2}Py_xRCOO_y^-$ combined with $(CH_3)_3COH$;[209] the complex $Fe_2O(OOCCH_3)_2Cl_2$. .$(bipy)_2$ together with $(CH_3)_3COOH$;[210] the complex $Fe_2O(bipy)_4Cl_4$ combined with H_2O_2.[211]

3. Certain other enzymes

A whole series of other enzymes containing metals capable of oxidising C–H compounds are known. They are less important than cytochrome P-450 and have been less thoroughly investigated. We shall list some of the enzymes and their models which oxidise hydrocarbons. Pteridine-dependent monoxygenases, which hydroxylate phenylalanine to tyrosine, containing non-haem iron, while the hydroxylase isolated from *Chromobacterium violaceum* incorporates copper.[212] Systems which have been known for a long time, such as Fenton's reagent, which includes iron(II), H_2O_2, and EDTA, Udenfrend's system containing iron(II), O_2, ascorbate, and EDTA, and Hamilton's system whose composition includes iron(III), O_2, and catechol, can serve as models of hydroxylases (with certain stipulations).[212] Ruthenium analogues of these systems have been proposed recently: ruthenium(III) together with H_2O_2, ascorbate, and EDTA [213] and ruthenium(III) with O_2, ascorbate, and EDTA.[214] Copper(I) complexes with chelating ligands are capable of hydroxylating the benzene ring of the ligand on treatment with O_2,[215,216] while on treatment with PhIO they promote the introduction of an OH group into the α-position in pyridine.[217]

Ketoglutarate-dependent dioxygenases oxidise C–H compounds in the presence of ketoglutaric acid which decomposes into succinic acid and CO_2 in a reaction coupled with the hydroxylation of the substrate.[1] A chemical model of such an enzyme, including an iron

compound and pyruvic acid, has been proposed.[218] In particular, catechol 1,2-oxygenase isolated from *Alcaligenes paradoxus* contains non-haem iron and catalyses the cleavage of the catechol ring.[219] A system consisting of a copper complex and an amine, which is capable of catalysing the oxidation of cyclohexanone, initially to α-hydroperoxycyclohexanone, is a model of pyrocatechase, a copper-containing dioxygenase.[220]

VI. Conclusion

The field of chemical science devoted to the activation of the C–H bond continues to develop vigorously. During the preparation of the manuscript for the press, several tens of articles describing a wide variety of processes occurring with the cleavage of the C–H bond and requiring the participation of metal complexes were published. Some of them are listed below.

Some of the communications describe the reactions of alkanes and arenes with complexes of metals in a low oxidation state, which proceed via the oxidative addition mechanism. Biscyclopentadienyltitanium(III) hydride complexes stimulate the deuterium–hydrogen exchange between methane and dihydrogen under mild conditions in solution in cyclohexane. Multiple exchange takes place in methane, while cyclohexane does not enter into the reaction.[221] The iridium-containing centre of the complex $[(PPh_3)_2IrH_2]_3PW_{12}O_{40}$ activates the C–H bond in arenes, alkanes, and allyl groups.[222] The methyl group of the substituent in a ruthenium-containing cluster undergoes oxidative addition to the ruthenium centre.[223] Oxidative addition of methane has been observed in the photolysis of the complex $CpIr(CO)H_2$ in a methane matrix at 12 K.[224] In the presence of silane, the complex $Cp_2Ta(CH_3)(PMe_3)$ reacts with benzene on photolysis (at 350 nm) or on heating (at 100 °C) with formation of methane and the compound $Cp_2Ta(C_6H_5)(PMe_3)$.[225] The silanes R_3SiH react with the hydride $ReH_7(PPh_3)_2$, which results in the cleavage of the Si–H bond and the formation of the derivative $ReH_6(SiR_3)(PPh_3)_2$ and H_2.[226] The formation of a η^2-arene complex with the $Cp^*Rh(PMe_3)$ species, which can be converted into the arylrhodium hydride $Cp^*Rh(PMe_3)(H)Ar$, has been observed.[227] The functionalisation of compounds containing C–H bonds by the insertion of the isonitrile group has been described. The complexes Cp^*ML_2 [228] or $RhCl(PR_3)_2(CNR')$ participate in this reaction.[229] The interaction of aromatic and aliphatic C–H bonds with terminal alkynes on photocatalysis by the complex $RhCl(CO)(PMe_3)_2$ results in the formation of 1,1-disubstituted ethylenes. Thus the reaction of n-hexane with phenylacetylene affords the product of the addition of hexane exclusively to the methyl group: 2-phenyloct-1-ene.[230] The intramolecular hydrogen transfer from the alkyl substituent of the phosphine ligand to the metal atom on UV irradiation of the $WH_4(PRPh_2)_4$ complexes was demonstrated even earlier and the possibility, in principle, of the photochemical activation of the methane bonds by the phosphinemolybdenum hydride complexes $MoH_4(PMePh_2)_4$ was demonstrated.[231] Cycloalkanes can be dehydrogenated under mild conditions in the presence of Group VIII metal complexes and active spongy uranium U*.[232] The interaction of the complexes $(PMe_3)_3RhMe$ with benzene or toluene at 70 °C results in the formation of the derivatives $(PMe_3)_3RhAr$.[233] The reactions of the radical species derived from the tetramesitylene-porphyrinatorhodium complex TMPRh* with methane in solution in benzene afford the complexes TMPRhMe and TMPRhH.[234] The organomagnesium compounds $C_6H_5Mg_nX$ (n = 2–4, X = halogen), formed on cocondensation of aryl halides and magnesium in the gas phase, react with alkanes even at room temperature. The degree of conversion of n-hexane per mole of the organomagnesium compound reaches 640. The composition of the products depends on the degree of reaction. A mixture of saturated C_4–C_8 hydrocarbons, mainly with a branched structure, is formed from n-hexane. With increase in the reaction time, the fraction of the C_4–C_8 products falls, but the yield of hydrocarbons containing eight and more carbon atoms increases.[235]

The mechanism of the reactions of low-valence metal complexes with alkanes and arenes has been investigated (see Ryabov's review[236]). Non-empirical calculations of the structure and relative energy characteristics of the ion-molecule complexes $Cu^+.CH_4$ and $Cu^+.C_2H_6$ have been performed. Tridentate coordination of the methane molecule is most favourable for the $Cu^+.CH_4$ ion. At moderately high temperatures, the Cu^+ cation is capable of quasi-free migration around the methane molecule.[237] Complexes of alkanes with the $W(CO)_5$ species in the gas phase[238] and the mechanism of the substitution of n-heptane by hex-1-ene in the photochemically generated species $[(n\text{-heptane})Cr(CO)_5]$ [239] have been investigated. The mechanisms of the cleavage of the Si–H bond by metal complexes has been discussed.[240,241] A detailed study has been devoted to the mechanism of the activation of C–H bonds in tetramethylsilane and mesitylene by tetrakis(triphenylphosphine)-hydridoneopentylosmium(II).[242] Finally, it has been shown that the reaction involving the photochemical dehydrogenation of alkanes in the presence of catalytic amounts of the complex $Rh(PMe_3)_2(CO)Cl$ begins with the abstraction of the CO ligand.[243]

Communications describing the oxidation of alkanes and arenes directly by high-valence metal complexes and also reactions occurring in the presence of such complexes have been published. The study[116,117] of the oxidative functionalisation of alkanes and arenes by palladium(II) acetate in trifluoroacetic acid has been continued.[244] It is essential to note that Stolyarov et al.[245] were unable to observe the oxidation of methane by a palladium(II) compound under the conditions described previously.[116,117,244] At the same time, methane is selectively oxidised by cobalt(III) trifluoroacetate with a 90 ± 10% yield of methyl trifluoroacetate relative to cobalt(III).[245] In the presence of palladium(II) acetate, cyclohexane and other alkanes are carboxylated with the aid of CO in CF_3COOH to cyclohexanecarboxylic and benzoic acids.[246,247] Irradiation of a solution of adamantane in acetonitrile with UV light under an oxygen atmosphere in the presence of palladium(II) or copper(II) trifluoroacetate leads to the formation of products resulting from the oxidation of mainly the third carbon atom.[248]

Irradiation with light of a solution of an alkane (or benzene) in CF_3COOH in the presence of the polyvanadate ions formed on dissolution of KVO_3 affords an alkyl trifluoroacetate and a ketone (or phenyl trifluoroacetate). When n-hexane is oxidised, the relative reactivities of the hydrogen atoms in the 3-, 2-, and 1-positions in n-hexane are 1.0 : 2.9 : 0.43.[249] Ruthenium(V) oxo-complexes oxidise cyclohexane and adamantane in solution in acetonitrile at 25 °C to cyclohexanone (yield 60% relative to the complex) and 1-adamantanol (40%) respectively.[250] Ruthenium(VI) and osmium(VI) dioxo-complexes oxidise alkanes on irradiation with light.[251] A number of studies have been devoted to the catalytic photochemical functionalisation of alkanes in the presence of polyoxometallates.[252–254] The photodimerisation of cyclohexene and methane on treatment with the $W_{10}O_{32}^{4-}$ ions has been investigated by the molecular orbital method.[255]

The heteropolyanion $SiRu(H_2O)W_{11}O_{39}^{5-}$ catalyses the oxidation of alkanes by persulphate, periodate, alkyl hydroperoxides, and iodosobenzene.[256] Chromium complexes catalyse the oxidation of adamantane by alkyl hydroperoxides.[257] Hydrogen peroxide in CF_3COOH in the presence of vanadium(5+) [136,137] oxidises even methane.[258] Alkanes are hydroxylated by periodate in the presence of $RuCl_3$ with the intermediate formation of RuO_4.[259] The rhodium complex of 1,2-bis(diphenylphosphino)ethane catalyses the oxidation of alkanes by hypochlorite.[260] *N*-Benzoyl-2-methylaniline is *ortho*-hydroxylated by trimethylamine oxide in the presence of a copper(II) salt with the intermediate formation of a copper(III) derivative.[261] The addition of iron(III) salts increases the quantum yields of the products of the photochemical hydroxylation of benzoic acid by hydrogen peroxide,[262] especially in the presence of methylene blue.[263] It has been concluded[264] that the abstraction of a hydride ion is the most likely mechanism of the activation of alkanes by carbonium ions and metal complexes — soft Lewis acids.

Reactions involving the oxidation of alkanes and arenes by molecular oxygen in the presence of metal complexes have been studied vigorously. It has been found that, in the gas-phase oxidation of propane (at 313 °C), the process is inhibited by the polyphthalocyanine complex of copper, whereas similar complexes of iron, cobalt, and manganese, present in small amounts, accelerate the reaction without altering the qualitative composition of the products. Analysis of the catalysts by EPR and IR spectroscopy demonstrated the absence of changes in their structure during the reaction.[265]

A whole series of studies have been devoted to the initiated radical chain oxidation of alkanes in the liquid phase[266–269] and also to cobalt bromide catalysis.[270] A trinuclear ruthenium carboxylate complex proved to be an effective catalyst of the oxidation of alkanes by atmospheric oxygen at 75 °C.[271] It has been concluded[272] that all the reactions of organic substrates with dioxygen are catalysed by metal ions which are bound to be present as impurities.

The photochemical oxygenation of alkanes and aromatic alkyl-substituted compounds by dioxygen catalysed by metal oxo-complexes, described in an earlier study[273] (see also Refs. 156–163), was developed in investigations by other workers.[274] A new system based on palladium acetate and phenanthroline, permitting the hydroxylation of benzene to phenol by molecular oxygen, was discovered.[275] Benzene is hydroxylated by dioxygen in the presence of palladium and copper complexes and molecular hydrogen.[276] The hydroxylation of benzene by dioxygen in the presence of $FeCl_3$, catechol, and pyridine in acetonitrile has also been described.[277] Finally, it has been found that methane is functionalised by cross-dimerisation with methanol in the reaction initiated by atomic oxygen; oxygen atoms are formed in their turn on interaction of photoexcited mercury atoms with N_2O.[278]

Detailed study of the Gif system[279–282] and of its models based not on dioxygen but on peroxides[283,284] and of the mechanism of the functioning of the system[285] has been continued. An analogous system incorporating a complex of iron with picolinic acid and dixoygen[286] or hydrogen peroxide[287] was proposed. Such systems can be regarded as models of oxygenases. The mechanism of the hydroxylation of aromatic compounds by the $Cu^+ - H_2O_2$ system has been discussed.[288]

Most communications have been devoted to the study of the biological and biomimetic oxidation of compounds at C–H bonds and several books have been published on this topic.[289–292] Attention has been concentrated on oxidation with participation of cytochrome P-450 [293–295] and also on the modelling of such processes (see the review of Mansuy et al.[296]), usually using porphyrin complexes of metals as catalysts.[297–306] It has been found that azidoporphyrinato-complexes and other complexes of chromium(III), manganese(III), and iron(III) catalyse the selective hydroxylation of alkanes at low temperatures by molecular oxygen in the absence of a reductant.[307–309] A fully inorganic model of cytochrome P-450 has been proposed in which the catalyst is iron deposited on a zeolite and the oxidation is effected either with H_2O_2 or with the $O_2 - H_2$ couple. In the oxidation of n-octane with participation of H_2O_2 on Fe/ZSM-5, the main product is 1-octanol.[310] The mechanism of the functioning of cytochrome P-450 and of its models has been discussed.[311–314]

The oxidation of 1,1-dimethylcyclopropane[315] and ethane[316] catalysed by MMO has been described. The substrate specificity in the oxidation by the soluble form of the above enzyme isolated from *Methyloccocus capsulatus* has been discussed in detail.[317] It was of interest that the hydroxylation of methane with participation of *Methylosinus trichosporium*, which leads to the formation of methanol, has been observed only when the microorganisms were treated with cyclopropane.[318] A dinuclear iron complex with bridging oxo-ligands can serve as a structural model of MMO.[319]

Photochemical models of the monoxygenase oxidation by dioxygen have been proposed,[320,321] the role of light consisting in exciting a sensitiser capable of generating the reducing component necessary for the reaction. The reactions involving biomimetic oxygenation by a system based on iodosobenzene and metal complexes with bleomycin, modelling cytochrome P-450, have been discussed.[322]

Data have been published on the oxidation of alkanes and arenes by other enzymes — hydroxylases,[323–327] dioxygenases,[328,329] and chloroperoxidase.[330] The reaction of dioxygen with a dinuclear copper(I) complex leads to the hydroxylation of the benzene ring of the ligand and can be regarded as a model of the process catalysed by tyrosinase[331] (see also Kitajima et al.[332]). The models of ligninase, a peroxidase which oxidises lignin (C–C bonds are then cleaved and the benzene rings are hydroxylated), are based on metalloporphyrin complexes and use hydrogen peroxide[333] or persulphate[334] as the oxidant. The model of the vanadium-containing bromoperoxidase includes a vanadyl complex,[335] while the complex $[Mn_4O_2(OCCPh_3)_6(H_2O)_2]$, modelling the oxygen-evolving centre of the photosystem II, catalyses the oxidation of alkanes by alkyl peroxides or iodosobenzene.[336] In the presence of a nitrogen-containing base in iron complexes with bisimidazolyl-methane, the methylene group is oxidised by atmospheric oxygen. Such complexes model the coordination of metal ions in certain metalloproteins, while the oxidation process itself may be similar to oxidation catalysed by lipoxygenases.[337] The complexes $V_2W_4O_{19}^{4-}$, $V_{10}O_{28}^{6-}$, and others catalyse the oxidative cleavage of catechol and model catechol dioxygenase.[338] Iron phenoxide complexes, obtained from Schiff bases, can serve as models of dioxygenases.[339] Finally, we may note that the insertion of oxygen into an aromatic ring, catalysed by complexes which are models of catechol dioxygenases, has been investigated by the extended Hückel method.[340]

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Polycondensation and polyaddition processes using silylated monomers

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ABSTRACT. Polycondensation and polyaddition reactions using silylated monomers are reviewed. Means of obtaining silylated nucleophilic monomers and the influence of silylation on the reactivity of nucleophiles containing amine, hydroxyl and thiol groups have been analysed. It has been shown that in many cases the use of silylated monomers enables polycondensation processes to be carried out under mild conditions to give high molecular systems.

The bibliography contains 88 references.

Contents

I. Introduction 868
II. Polycondensation reactions using silylated nucleophiles 868
III. Polycondensation reactions in the presence of silylating agents 881

I. Introduction

Polycondensation chemistry has been enriched in the last two decades by a series of new processes which significantly broaden the scope of linear polycondensation and polycyclocondensation. These include 'direct' polycondensation,[1,2] 'activated' polycondensation,[3] polycondensation using phase transfer catalysts,[4] reductive polyheterocyclisation,[5,6] etc. Polycondensation processes using silylated monomers,[7–10] also called 'silylated' polycondensation,[10] must be included. 'Silylated' polycondensation, like 'direct'[1,2] and 'activated'[3] polycondensation is based on a change, usually an increase, in the reactivity of one of the monomers participating in the reaction, however, in contrast to the processes mentioned above, 'silylated' polycondensation assumes a change of reactivity in electrophilic and nucleophilic monomers including diamines, bis-phenols, bis-thiophenols and multifunctional systems.[10]

This approach was used for the first time in synthetic chemistry by Klebe and collaborators[7,8] from the middle sixties to the beginning of the seventies and has been taken up once more in the last 5–10 years. Some achievements in the area of 'silylated' polycondensation have been considered,[7–10] however none of these reviews gives a complete picture of the achievements of this rapidly developing area of polycondensation. The present review is required to fill this gap.

II. Polycondensation reactions using silylated nucleophiles

1. Methods of obtaining silylated nucleophilic monomers

The silylation of nucleophilic monomers reduces to the protection of labile hydrogen atoms in their functional groups by tris-(hydrocarbonyl)silyl residues, most frequently by trimethylsilyl or dimethylphenylsilyl groups.

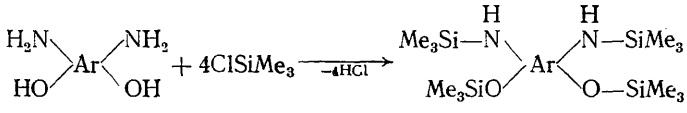
The most widespread method of silylating nucleophiles is treatment of them with chloro-tris(hydrocarbonyl)silane, most frequently with chlorotrimethylsilane in inert solvents in the presence of acceptors of the hydrogen chloride released

$$HX{-}Ar{-}XH + 2Cl{-}SiR_3 \xrightarrow{-2HCl} R_3Si{-}X{-}Ar{-}X{-}SiR_3,$$
$$X = {-}NR'{-},\ {-}O{-},\ {-}S{-};\ R' = {-}H,\ {-}C_6H_5$$

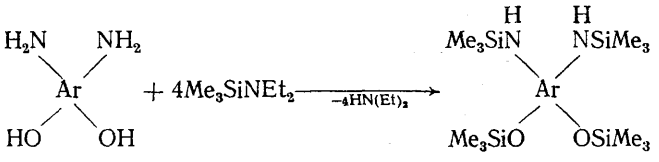
This method has been used successfully for the silylation of primary diamines,[11–13] secondary diamines,[12–14] bis-phenols[15–17] and bis-thiophenols.[18] The silylation of secondary diamines, bis-phenols and bis-thiophenols leads to a bis-silylated product while analogous conversions of primary diamines may, depending on the conditions of carrying out the reaction, lead to the preparation of both bis-silylated[11–13] and *N,N,N',N'-tetrakis*-silylated diamines[19]

$$Me_3SiN{-}Ar{-}NSiMe_3 \leftarrow H_2N{-}Ar{-}NH_2 \rightarrow$$
$$\rightarrow (Me_3Si)_2N{-}Ar{-}N(SiMe_3)_2.$$

The same method of silylation was successfully used for obtaining *N,N',O,O'-tetrakis*-(trimethylsilyl)-bis(*o*-aminophenols)[20]



An alternative method of silylating bis-(*o*-aminophenols) is based on the use of trialkylsilyldialkylamines,[21–24] particularly of trimethylsilyldiethylamine in place of chlorotrimethylsilane



The last method has several significant advantages over silylation with chlorotrimethylsilane, such as reaction being effected in an excess of trialkylsilyldialkylamine in the absence of solvent and HCl

acceptor since the reaction byproduct is diethylamine. It is interesting to note[24] that on silylation of aminophenols the phenolic hydroxyls reacted first which made possible the isolation and characterisation of the *o*-, *m*- and *p*-isomers of the following series of compounds:

$$Me_3SiOC_6H_4\overset{H}{N}H_2,\quad Me_3SiOC_6H_4\overset{H}{N}SiMe_3,\quad Me_3SiOC_6H_4N(SiMe_3)_2.$$

Finally, silylated bis-phenols are obtained by treating various bis-phenols with hexamethyldisilazane in inert solvents[16]

$$HO—Ar—OH + Me_3Si\overset{H}{N}SiMe_3 \xrightarrow[-NH_3]{} Me_3SiO—Ar—OSiMe_3.$$

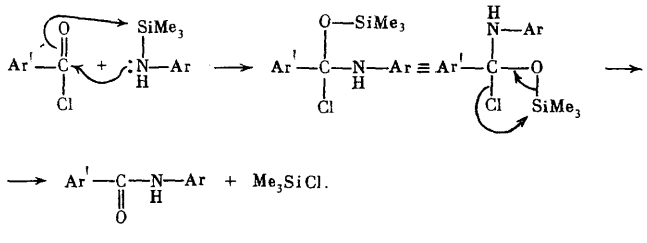
The same approach was used to obtain silylated derivatives of hydroxybenzoic acids[16]

$$HO—Ar—\overset{O}{\overset{\|}{C}}—OH + Me_3Si\overset{H}{N}SiMe_3 \xrightarrow[-NH_3]{} \rightarrow Me_3SiO—Ar—\overset{O}{\overset{\|}{C}}—OSiMe_3.$$

2. Reactivity of silylated nucleophilic monomers

As mentioned above the silylation of nucleophilic monomers is accompanied by a change in their reactivity. This problem has been considered in greatest detail when applied to silylated primary amines which possess an increased reactivity in reactions with carboxylic acid chlorides. The high reactivity of *N*-silylated amines may be explained by means of the mechanism presented below.[25]

It is a characteristic of organosilicon compounds that Si atoms have a high affinity for oxygen, and for fluoride and chloride ions and also that a carbocation in a position 3 to silicon may be stabilised by the $\sigma-\pi$ effect of the latter. A two-stage addition-elimination mechanism has been proposed for the nucleophilic substitution of acyl in acid chlorides by an *N*-trimethylsilylated amine allowing for these special features of organosilicon compounds[25]



In the first stage of the reaction, attraction of the carbonyl oxygen of the acid chloride for the Si atom of the *N*-silylated amine facilitates nucleophilic attack by the nitrogen atom of the latter on the carbonyl carbon of the acid chloride, with subsequent rapid formation of a tetrahedral intermediate. In the second stage of the process elimination of a chloride ion from the intermediate is facilitated by the presence of the Si atom in the β-position which leads to rapid formation of amide together with chlorotrimethylsilane.[25]

The reactivity of *S*-trialkylsilated thiophenols may approach the reactivity of *N*-silylated amines.[18] Silylation of a hydroxyl group leads to its protection from electrophilic attack[8,26] as a result of the strong affinity of silicon for oxygen.

The reactivity of *S*-trimethylsilylbenzenethiol (I), *N*-trimethylsilylaniline (II) and *O*-trimethylsilylphenol (III) towards electrophiles has been compared.[18] It was found that the relative reactivities of these compounds on reaction with benzoyl chloride is expressed in the series (II) > (I) > (III) and in reaction with 1-chloro-2,4-dinitrobenzene in the series (I) > (II) > (III). *O*-Trialkylsilated phenols (trialkylsilyloxybenzenes) may react with such electrophiles as acid halides and activated organic halides only in the presence of chloride or fluoride ion

$$Ar—O—SiMe_3 + X^{\ominus} \rightarrow Ar—O^{\ominus} + Me_3SiX.$$

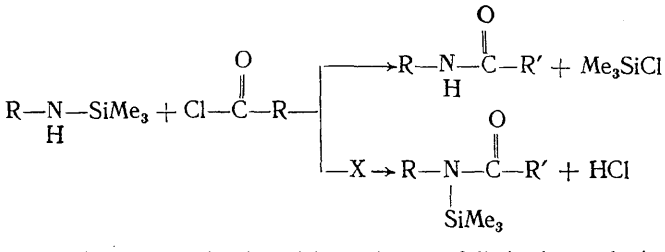
The silylation of such tetrafunctional nucleophiles as bis-(*o*-aminophenols) leads, in full agreement with that mentioned above, to activation of amino and deactivation of hydroxyl groups,[20] which facilitates[27,28] the selective execution of the first stage of polycyclocondensation and permits avoidance of gel formation.

3. Condensation and addition polymers based on silylated diamines

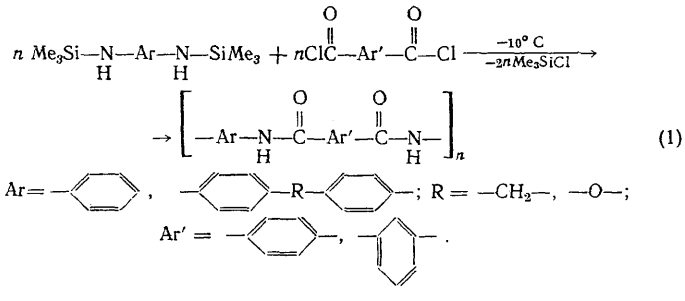
As was shown above *N*-trialkylsilylated amines are some of the most reactive organosilicon compounds. They react with various electrophiles such as acid chlorides and anhydrides, isocyanates, benzyl halides, aldehydes, etc.[8] All these reactions have been used to obtain nitrogen-containing condensation and addition polymers.[10]

a) Synthesis of polyamides

It is known[29] that on reacting *N*-trimethylsilyl-protected amines with carboxylic acid chlorides, amides are formed with the elimination of chlorotrimethylsilane as byproduct and not trimethylsilylamides with elimination of hydrogen chloride as a byproduct



This amidation reaction is widely used successfully in the synthesis of polyamides. Thus high molecular aromatic polyamides have been obtained[25,30] by the interaction of *N,N'*-disilylated aromatic diamines with diacid chlorides of aromatic dicarboxylic acids under low temperature polycondensation conditions in solution

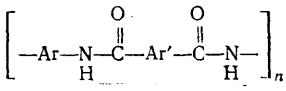


(1)

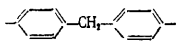
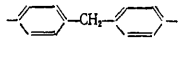
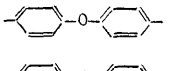
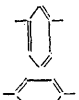
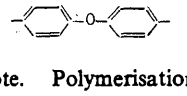
Comparison of the polyamidation process being considered with the traditional method of synthesis of aromatic polyamides, viz. reaction of diamines with diacid chlorides of dicarboxylic acids,[31–33] using the synthesis of poly-(*p*-phenyleneterephthalamide) as example, showed[30] that *N,N'*-disilylated *p*-phenylenediamine

reacts much more rapidly with terephthaloyl chloride. Polyamides with higher viscosity characteristics are obtained. Some results of syntheses of aromatic polyamides are shown in Table 1.

Table 1. Viscosity characteristics of aromatic polyamides of formula



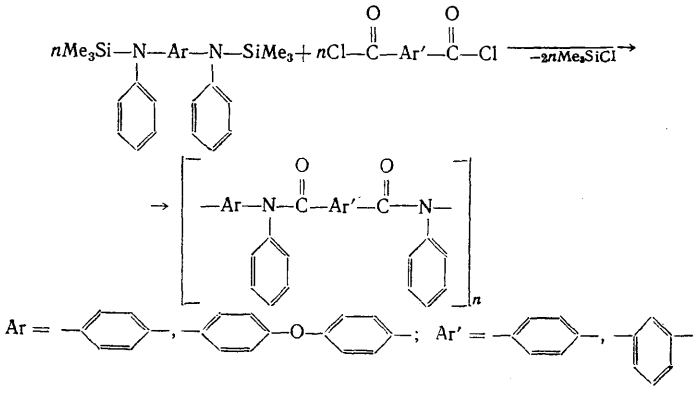
(Ref.25)

Ar	Ar′	η_{inh}, dlitre g^{-1}, conc. H_2SO_4, 30 °C	
		from *N*-silylated diamines	from unsilylated diamines
		2.45	1.03
		3.19	0.94
	 *	7.41	3.23
		2.41	1.19
		2.54	1.15
		3.21	1.40
		3.97	2.10
		3.99	1.50

Note. Polymerisation was carried out in *N*-methyl-2-pyrrolidone (NMP) containing LiCl, at −10 to −5 °C for 5 h.
*Polymerisation was carried out in a mixture of NMP and hexamethylphosphoramide (HMPA) containing LiCl at −10 to −5 °C for 12 h.

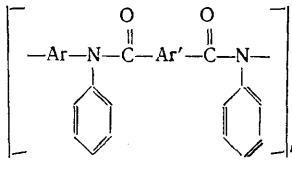
Analysis of the data shown in Table 1 indicates that without exception polyamides are obtained with significantly higher viscosity characteristics from silylated diamines than from free diamines.

The use of silylated diamines is particularly expedient in those cases when high molecular compounds cannot be obtained from free monomers of this class. The preparation of high molecular polyamides based on weakly basic diamines, which have low reactivity, is extremely problematical. The *N*-silylation of such diamines is a reliable method of activating them[12,13,34] and may be illustrated using aromatic *N,N′*-diphenyl-substituted diamines as an example.[13,34,35] These compounds, being extremely low in reactivity, are activated by silylation to such an extent that their reaction with diacid chlorides of aromatic dicarboxylic acids under high temperature polycondensation conditions in tetramethylene sulphone leads to the formation of high molecular poly-(*N*-phenyl)amides:[13,34,35]

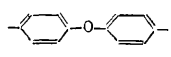
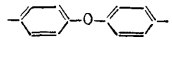


Some characteristics of the poly-(*N*-phenyl)amides synthesised are given in Table 2.

Table 2. Conditions of synthesis and viscosity characteristics of poly-(*N*-phenyl)amides of general formula



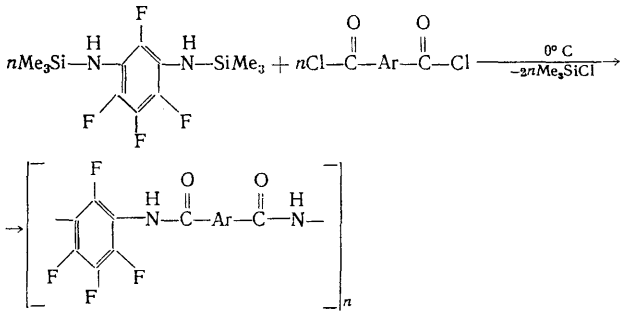
(Refs.13, 34)

Ar	Ar′	Polycondensation conditions		η^*_{inh}, dlitre g^{-1}	T_g^{**}, °C
		T, °C	time, h		
		160	24	1.65	225
		200	6	2.21	255
		160	24	1.24	195
		200	24	1.35	215

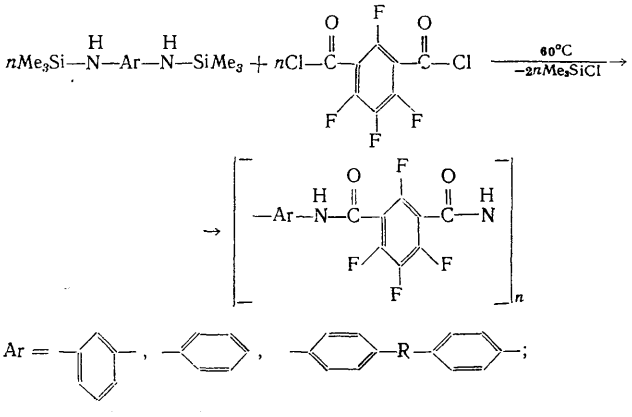
*η_{inh} was measured in H_2SO_4 at 30 °C and a concentration of 0.5 g dlitre^{-1}; ** T_g was determined by differential thermal analysis (DTA) at a heating rate of 10 °C min^{-1}.

Analysis of the data given in Table 2 indicates that, as in the processes considered above for unsubstituted polyamides, the use of *N*-silylated diamines made it possible to obtain systems with extremely high viscosity characteristics. The poly-(*N*-phenyl)amides synthesised had T_g 195–255 °C. They dissolved in various solvents, including dimethylformamide (DMF), *m*-cresol and chloroform.

Tetrafluoro-*m*-phenylenediamine is a diamine with low basicity. It too may be activated by silylation.[36] High molecular fluorine-containing polyamides are obtained by reacting its *N,N'*-bis-trimethylsilylated derivative with diacid chlorides of aromatic dicarboxylic acids under low temperature polycondensation conditions in solution



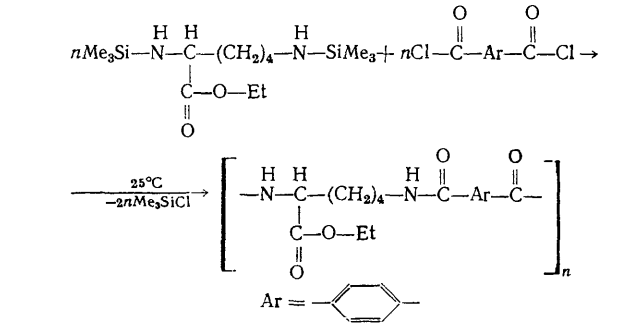
It is interesting to note that silylated aromatic diamines form high molecular polyamides even on reaction with the poorly reactive diacid chlorides of aromatic dicarboxylic acids. The preparation of fluorine-containing polyamides by reaction of *N*-silylated aromatic diamines with tetrafluoroisophthaloyl chloride under low temperature polycondensation conditions in solution is an example[37]



R = —O—, —CH_2—.

Fluorine-containing aromatic polyamides obtained by a scheme analogous to this possessed η_{inh} equal to 0.43 dlitre g^{-1} and T_g equal to 245–280 °C (Table 3).

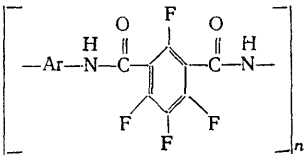
In addition to aromatic systems, aliphatic-aromatic polyamides have also been obtained based on *N*-silylated diamines. In particular high molecular aliphatic-aromatic polyamides are obtained by the polycondensation of *N*-silylated lysine with the diacid chloride of an aromatic dicarboxylic acid:[38]

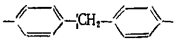
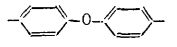


Polyterephthalamides obtained from *N*-silylated lysine possessed η_{sp} = 1.02 [hexamethylphosphoramide (HMPA)].[38]

The interaction of silylated diamines with diacid chlorides according to Scheme (1) may be effected not only in solvents but also under conditions of solvent-free vacuum 'deposition' polycondensation (from the gas phase) making it possible to obtain thin films on appropriate substrates.[39] Thin polyamide films may also be obtained using unsilylated diamines[40,41] however a temperature of the order of 100 °C is required to remove the HCl formed during the reaction. On using *N*-silylated diamines the solvent-free vacuum 'deposition' polycondensation from the gas phase takes place at temperatures of the order of 60 °C with separation of neutral chlorotrimethylsilane. Metallic plates capable of erosion may be used as substrates and are coated with thin polyamide films. It is interesting to note that poly-*p*-phenyleneterephthalamide (Kevlar), usually a highly crystalline polymer, applied using silylated diamine, forms an amorphous transparent film.

Table 3. Some characteristics of polyamides of general formula


(Ref.37)

Ar	η^{*}_{inh}, dlitre g^{-1}	T^{**}_{g}, °C
	0.43	245
	0.56***	275
	0.63	280
	0.82	280

Note. Polyamide synthesis was effected in chloroform containing triethylamine hydrochloride at 60 °C for 6 h.

* η_{inh} was measured for 0.5% solutions in DMA at 30 °C;

** determined by DTA at ΔT = 10° min^{-1} (air);

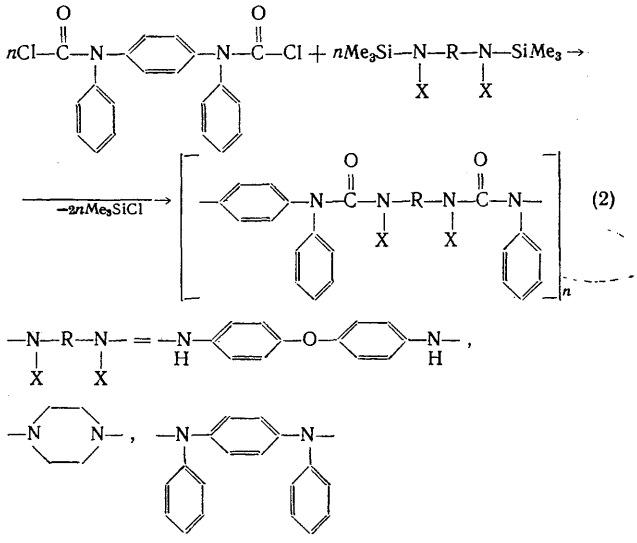
*** polycondensation was carried out at 0 °C for 6 h.

'Activated' polycondensation reactions[3] have been used for obtaining polyamides in addition to the reactions of silylated diamines with diacid chlorides. In particular silylated diamines react with bis-(2,4-dinitrophenyl) esters of dicarboxylic acids.[38] These processes, accompanied by the separation of *O*-silylated 2,4-dinitrophenol as a byproduct, are examples of polycondensation reactions using both activated nucleophiles and electrophiles. The examples given above demonstrate the application of polycondensation with silylated diamines to the efficient preparation of various polyamides.

b) Synthesis of polyureas

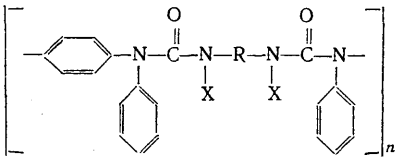
Silylated diamines have been used for obtaining polyureas by applying both polycondensation[12] and polyaddition[42] processes.

In particular, the reaction of *N,N'*-di(trimethylsilylated) aromatic diamines with *N,N'*-dichloroformyl-*p*-dianilinobenzene[12] proceeded according to Scheme 2 and *N*-phenylated polyureas were partially or completely obtained. Conditions of syntheses and individual characteristics are given in Table 4.

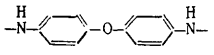
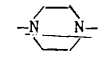
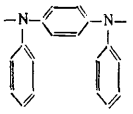


(2)

Table 4. Conditions of synthesis and some characteristics of polyureas of general formula



(Ref.12)

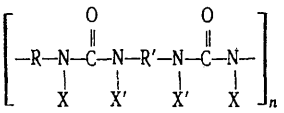
—N—R—N— (X, X)	Polycondensation conditions*			Properties of polymers	
	solvent	*T*, °C	time, h	yield, %	η_{inh}, dl·g^{-1}**
	*sym*-TCE	120	5	80	0.13
	anisole	120	5	80	0.19
	o-dichlorobenzene	120	5	78	0.12
	nitrobenzene	120	5	80	0.19
	sulpholan	120	5	88	0.22
	"	120	24	88	0.27
	"	180	5	79	0.09
	sulpholan	80	24	92	0.22***
	"	120	3	85	0.21***
	"	160	24	85	0.35***
	"	200	24	82	0.26***
	sulpholan	190	24	75	0.08
	"	220	5	76	0.09
	"	220	24	82	0.13
	"	250	24	70	0.09

* Polycondensation was carried out by reacting 1 mmole *N,N'*-dichloroformyl-*p*-dianilinobenzene with 1 mmole silylated diamine in 3 ml solvent in a stream of N_2;

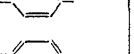
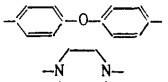
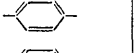
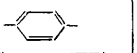
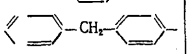
** viscosity was measured for 0.5% solutions in NMP at 30 °C;

*** viscosity was measured in conc. H_2SO_4.

Table 5. Thermal characteristics of polyureas of general formula



(Ref.12)

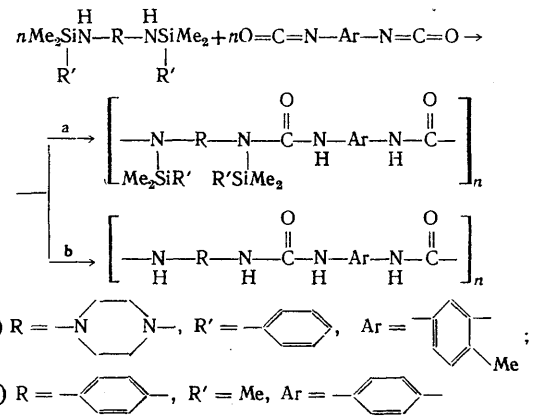
R	R'	X	X'	T_{dec}, °C* in air	T_{dec}, °C* in N_2
			H	265	295
		»	H	385	420
		»		520	520
	»	H	H	335	340

* T_{dec} is temperature at which polymer mass has lost 10% (TGA, ΔT = 10 °C min^{-1}).

As follows from analysis of the data given in Table 4 high molecular polymers were obtained in only one case, however the favourable influence of silylation of amines was recorded in the viscosity characteristics of the polyureas. Polymers with significantly lower viscosity characteristics were obtained from unsilylated diamines. The completely and partially phenylated polyureas obtained from silylated aromatic diamines dissolved readily in organic solvents such as dimethylacetamide (DMA), tetrahydrofuran (THF) or *m*-cresol and surpassed significantly in solubility the unsubstituted aromatic polyureas and also polymers from silylated piperazine, which are crystalline systems.

The introduction of phenyl substituents in place of comparatively labile hydrogen atoms into polyureas increases not only the solubility but also the thermal stability of these systems (Table 5) which is in agreement with the results of investigations on various classes of heterochain and heterocyclic polymers.[43]

An additional method of synthesising polyureas using silylated diamines was described by Klebe in 1964.[42] It was shown that addition of *N,N'*-disilylated diamines to a diisocyanate led to the preparation of *N*-silylated polyureas which were readily methanolised into unsubstituted polyureas



a) R = , R' = , Ar = ;

b) R = , R' = Me, Ar =

The polyaddition reaction occurs under homogeneous conditions even on carrying it out in non-polar solvents (Table 6) due to the lower polarity of *N*-silylated polyureas compared to unsubstituted polyureas.[44]

Table 6. Synthesis of aromatic polyureas in various solvents.[44]

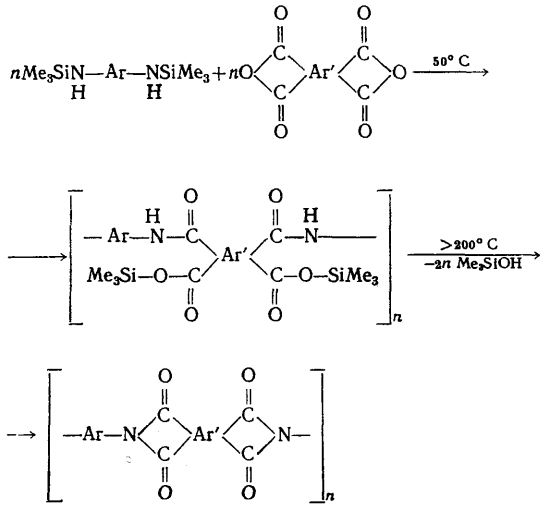
Solvent	η_{inh}, dlitre g^{-1}
DMSO	0.54
Tetramethylenesulphone	0.60
Tetrachloroethane (TCE)	0.91
Anisole	0.77
Nitrobenzene	0.65
Toluene	0.74

Note. Reaction of *N,N'*-bis(trimethylsilyl-substituted 4,4'-diaminodiphenylether was carried out at 100 °C for 10 h; viscosity was measured for 0.5% solutions in conc. H_2SO_4 at 30 °C.

It should be mentioned that polyureas obtained by the methanolysis of *N*-silylated polymers are characterised by low crystallinity and good solubility in organic solvents in difference to polyureas obtained by the usual method (diamines with diisocyanates).

c) Synthesis of polyimides

By analogy with the widespread two-step method of synthesis of polyimides[45–50] their preparation from silylated diamines occurs through the formation of intermediate polymers which are converted thermally into the desired systems.[51,52] The polyaddition of *N*-silylated aromatic diamines to dianhydrides of aromatic tetracarboxylic acids occurs with ring fission of the latter with the formation of trimethylsilyl esters of polyamidoacids which then form imides at a temperature >200 °C with the separation of trimethylsilanol



The presence of trimethylsilyl groups in the polyamidoacid esters determines the significantly greater stability of these polymers compared to unsubstituted polyamidoacids and also their increased solubility in non-polar solvents. The latter circumstance enables the synthesis of similar polymers not only in dipolar aprotic solvents of the type of DMA and *N*-methylpyrrolidone (NMP) but also in ethers or hydrocarbons. In several cases these processes are accompanied by precipitation of the polyamidoacid from solution (Table 7), however polyamidoacids with high inherent viscosities were obtained in practically all the solvents tested (Table 7).

Table 7. Synthesis of polyamidoacids in various solvents.[52]

Solvent	η_{inh}, dlitre g^{-1}	Reaction conditions
DMA	1.77	P
NMP	1.46	P
bis-Methoxyethyl ether	0.92	P
1,4-Dioxan	0.80	P
THF	0.97	P
Chloroform	0.99	P
Acetonitrile	0.88	O
Nitrobenzene	0.81	O
Toluene	0.92	O

Note. Synthesis of polyamidoacids was carried out by reacting *N,N'*-bis-(trimethylsilyl)-substituted bis-(4-aminophenyl)ether with pyromellitic anhydride at 20 °C for 1 h and then at 50 °C for 12 h; inherent viscosities were measured for 0.5% solutions in DMA at 30 °C; P denotes reaction in solution; O denotes formation of solid during reaction.

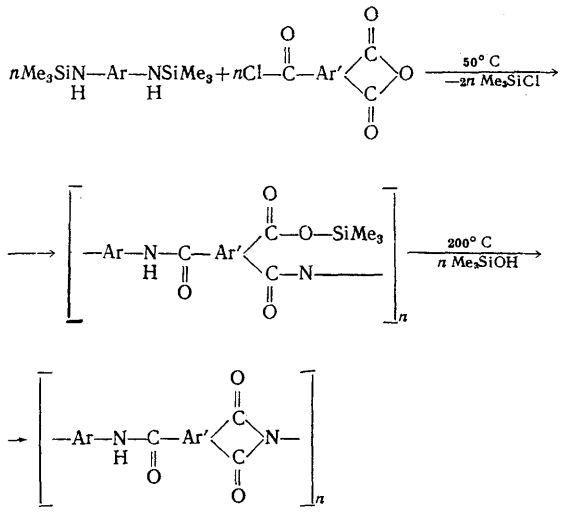
The thermal conversion of silylated polyamidoacids into polyimides occurs slowly and completion of imide formation requires higher temperatures compared with the cyclisation of unsubstituted polyamidoacids.

A single-stage process for synthesising polyimides using *N*-silylated diamines[53–55] has been applied to obtain polyimides containing residues of aliphatic diamines and polyimides difficult to obtain as high molecular systems from unsubstituted aliphatic diamines.[54] In addition these processes were used successfully to obtain polynaphthylimides distinguished by an enhanced stability towards hydrolysis.[56]

The synthesis of polyimides using *N*-silylated diamines, as when using unsubstituted diamines, may (by analogy with that suitable for polyamides[39] considered above) be used for applying thin films to appropriate substrates using solvent-free vacuum 'deposition' polycondensation from the gas phase.[57–59] In the first stage of applying thin polyimide films, the aromatic diamine and dianhydride are applied to the substrate under high vacuum which is then heated to effect imide formation.

Polycondensation using *N*-silylated diamines may also be used when appropriate with derivatives of aromatic polycarboxylic acids containing various electrophilic functional groups. Thus the

interaction of 4-chloroformylphthalic anhydride with *N,N'*-bis-(trimethylsilyl)-substituted 4,4'-diaminodiphenyl ether proceeded through a polycondensation/polyaddition reaction with the formation of the trimethylsilyl esters of polyamidoacids[60]



Results of the synthesis of intermediate polymers in various solvents are given in Table 8.

Table 8. Synthesis of copolyamido-amidoacids in various solvents.[60]

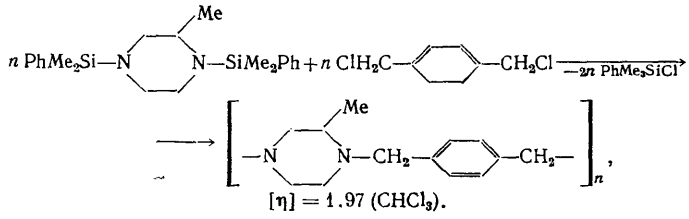
Solvent	η^{*}_{inh}, dlitre g^{-1}	Reaction conditions
DMA	1.82	P
NMP	1.48	P
Acetonitrile	1.14	O
Nitrobenzene	1.21	O
bis-Méthoxyethyl ether	1.00	O
1,4-Dioxan	0.75	O
THF	0.94	O
Chloroform	0.59	O
Benzene	0.57	O

Note. Synthesis was effected by reacting *N,N'*-bis-(trimethylsilyl)-substituted 4,4'-diaminodiphenyl ether with 4-chloroformylphthalic anhydride at −5 °C for 1 h and then at 50 °C for 4 h.
* Inherent viscosities were measured for 0.5% solutions in NMR at 30 °C.

As is seen from Table 8 only reactions in NMP and DMA media proceed homogeneously. Nonetheless polymers were obtained in practically all solvents with comparatively high solution inherent viscosity. The silylated intermediate polymer may be converted into a polyamidoimide by thermal treatment under the same conditions used in the synthesis of polyimides.

d) Synthesis of polyamines

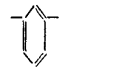
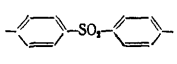
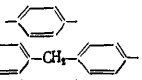
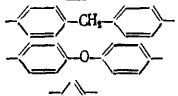
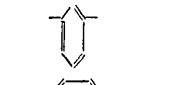
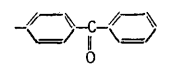
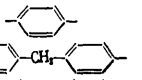
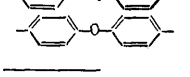
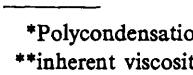
In spite of the fact that alkyl halides are aminolysed with difficulty compared with carboxylic acid chlorides, they may also interact with *N*-silylated amines.[8] According to Klebe[14] benzyl chloride reacts with *N*-silylated amines at temperatures >100 °C forming benzylamines and trialkylsilyl chloride in quantitative yield. Ammonium salts and cyclic sulphone catalytically increase the rate of the process. This reaction was extended to the synthesis of polyamines which are difficult to obtain as high molecular compounds by the reaction of diamines with dihalo compounds because of side reactions. Polycondensation of reactive dihalides of the benzyl chloride type with *N*-silylated piperazine, carried out in bulk at 150 °C, led to the formation of a high molecular polyamine[14]



$[\eta] = 1.97$ ($CHCl_3$).

Table 9. Conditions of synthesis and viscosity characteristics of aromatic polyamines of general formula

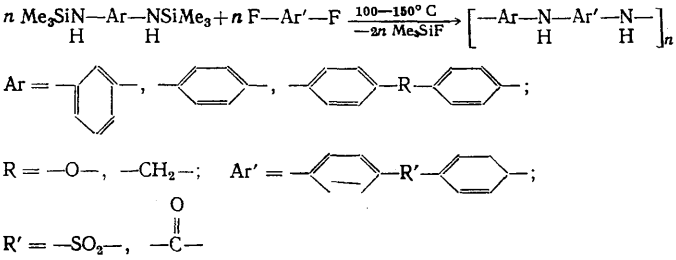
$$\left[-Ar-\underset{H}{N}-Ar'-\underset{H}{N}-\right]_n$$ (Ref.61)

Ar	Ar'	Polycondensation conditions* (temperature/time, °C/h)	η_{inh}, **dlitre g^{-1}
		100/7—150/14	0.62
	»	150/12	0.57
	»	150/12	0.42
	»	100/7—150/14	0.60
		100/24—240/48***	0.55
	»	220/48***	0.37
	»	100/24—240/48	0.45
	»	150/48	0.66

*Polycondensation was carried out in the presence of KF;
**inherent viscosities were measured for 0.5% solutions in NMP at 30 °C;
***polycondensation in tetramethylenesulphone.

A similar substitution reaction occurs on treatment of activated haloaromatic compounds with *N*-silylated aromatic amines. In this way secondary aromatic amines were formed together with

trimethylsilyl halides.[61] Correspondingly new aromatic polyamines were successfully obtained from activated aromatic difluoro compounds and *N*-silylated aromatic diamines[61]



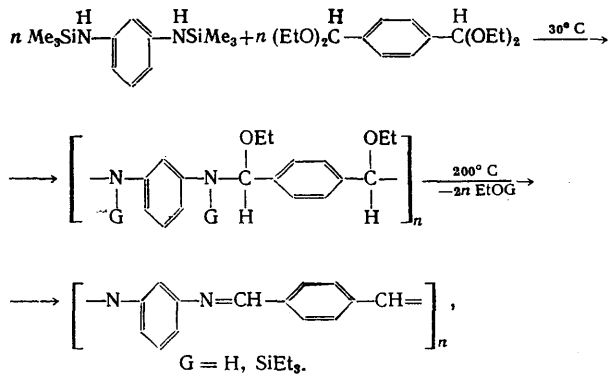
The polycondensation reaction was carried out in DMSO in the presence of fluorine-containing catalysts (KF, CsF) at 100–150 °C. Polyamines with comparatively high viscosity characteristics were obtained as a result (Table 9).

The presence of a catalyst is essential to obtain high molecular polyamines. The use of the corresponding dichlorides in place of activated aromatic difluorides led to the preparation of only low molecular polymers. Introduction of a nitro substituent into aromatic dihalo compounds increased their reactivity and led to the formation of polyamines with higher inherent viscosities. These aromatic polyamines dissolved readily in organic solvents like NMP and had $T_g \sim 200$ °C. They are potential engineering plastics.[61]

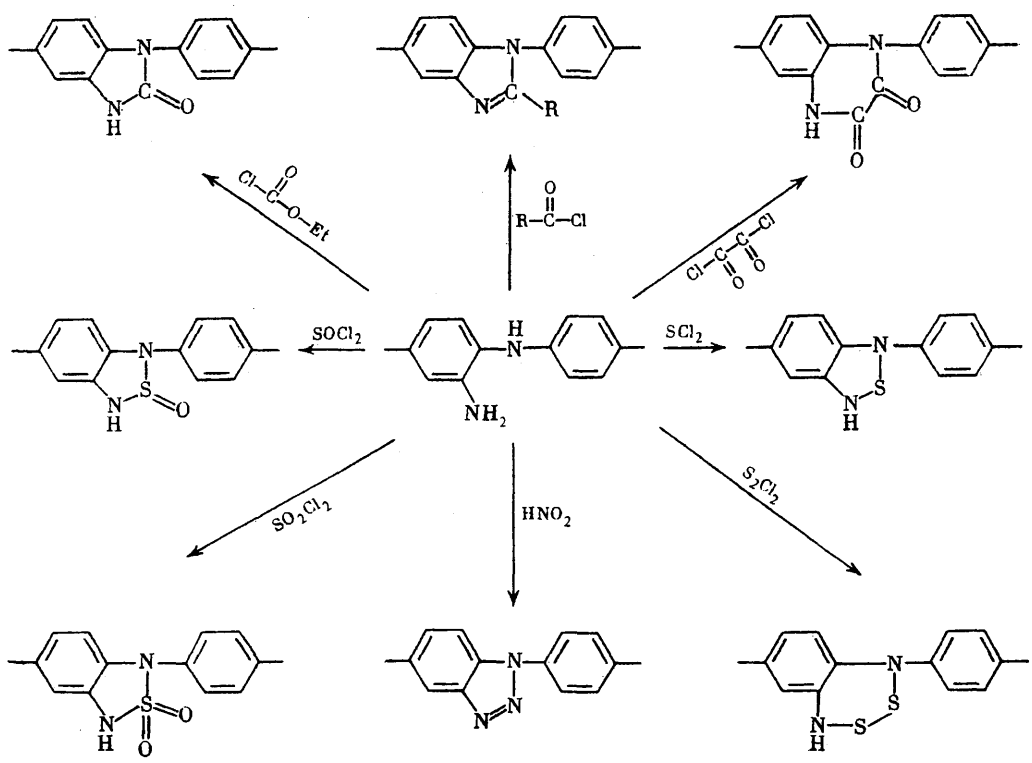
At the same time they may readily be reduced to the corresponding poly-(*o*-amino)amines[5,6,61–65] which in their turn may be used to obtain a large range of heterocyclic polymers[65]

e) Synthesis of polyazomethines

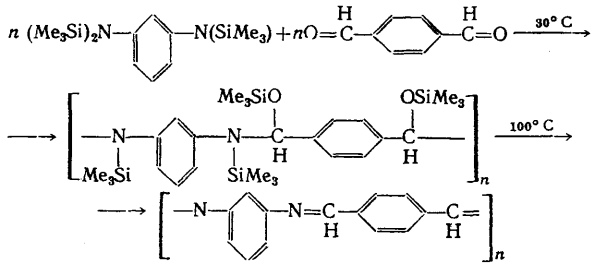
The majority of aromatic polyazomethines are not obtained as high molecular compounds because of their insolubility and infusibility. Kurosaki and collaborators[16,66] have intensively investigated reactions to obtain aromatic polyazomethines and found new synthetic routes to these systems using *N*-silylated aromatic diamines. One method led to the polycondensation reaction of *N,N'*-bis-(trimethylsilyl)-substituted aromatic diamines with aromatic bis-(diethylacetals) in NMP leading to an intermediate polymer which was soluble in organic solvents. This was reprocessed into films by conversion at 200 °C into insoluble polyazomethines[66]



Another method is the polyaddition of *N,N,N',N'-tetrakis*-(trimethylsilyl)-substituted aromatic diamines with aromatic dialdehydes in NMP with the formation of soluble intermediate polymers, with



subsequent conversion (thermal) into insoluble polyazomethine films[19]



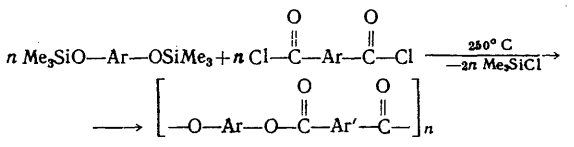
Similar intermediate polymers were formed in both cases in the first stages subsequently undergoing β-elimination with the formation of azomethine bonds in the main macromolecule chains.

4. Polymers based on *O*-silylated bis-phenols

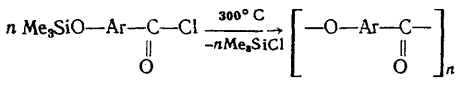
The possibility of using *O*-silylated bis-phenols to obtain high molecular compounds has been studied in detail by Kricheldorf and collaborators[15–17,67–70] who synthesised high molecular polyesters and polyethers based on these monomers.

a) Synthesis of polyesters

The possibility was shown in 1979 of synthesising polyaryl esters from *O*-silylated bis-phenols and diacid chlorides of dicarboxylic acids[15]



or from trimethylsilyloxybenzoyl chlorides

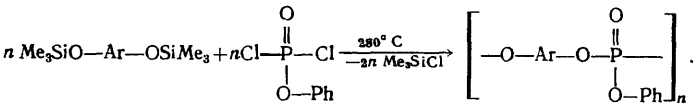


by polycondensation in bulk at 200–300 °C.

The drawback of the thermal polycondensation of two different monomers (A–A and B–B types) such as *O,O'*-trimethylsilyl-substituted 2,2-bis-(4-hydroxyphenyl)propane and isophthaloyl chloride is the possibility of distilling or subliming out the more volatile monomer which disturbs the stoichiometry of the starting materials and leads to a reduction in the degree of polymerisation. This drawback is eliminated in the homocondensation of monomers of the A–B type such as trimethylsilyloxybenzoyl chloride. The molecular weight of a polymer obtained from a *m*-hydroxybenzoic acid derivative (type A–B) was greater than that of a polymer from *O*-silylated bis-phenol and isophthaloyl chloride. Thus the silylation method is useful for the high temperature preparation of polyarylates from monomers of type A–B.

The homocondensation reaction of *m*- and *p*-silyloxybenzoyl chlorides has been carried out in bulk and in solution.[67,68] Polycondensation of *m*-trimethylsilyloxybenzoyl chloride in bulk at 250 °C led to the preparation of a polyaryl ester of molecular weight 10000–14000,[67] while polycondensation of the *p*-isomer in a high boiling solvent at 320 °C led to the preparation of a polymer of molecular weight 20000–50000.[68] In the latter case crystalline oligomers separated from solution in the first stage of the polycondensation, the molecular weight of which continued to grow on heating. Polycondensation was accelerated by such catalysts as triethylamine hydrochloride and benzyltriethylammonium chloride leading to polyaryl esters with large molecular weights.

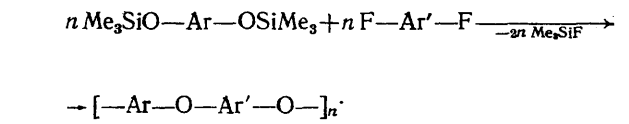
O-Silylated bis-phenols also react with aryl phosphodichloridates with the formation of aromatic polyphosphates which are polyesters in the wide sense of the word[69,70]



Polycondensation in bulk was carried out at 180–300 °C in the presence of catalytic amounts of benzyltriethylammonium chloride. Polyphosphates of molecular weight up to 12000 were obtained in this way.

b) Synthesis of polyethers

The possibility of using *O,O'*-bis-trimethylsilylated bis-phenols to obtain polyethers in addition to polyesters has been investigated.[16,17,71,73] Activated difluoro-aromatic compounds were selected as comonomers of silylated bis-phenols



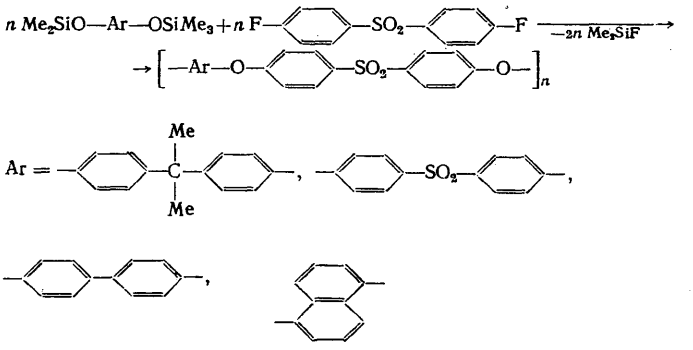
The use of the corresponding derivatives of the diphenylsulphone[16] and benzophenone[17] series as activated difluoro-aromatic compounds enabled the preparation valuable poly(ether sulphones)[16,72] and poly(ether ketones).[17,73]

These polymers are usually obtained by high temperature polycondensation of bis-phenols with activated dihalo-aromatic compounds in solutions of alkali metal salts.[74–78] The main drawback of these processes is the need to purify the desired polymers from reaction by products, viz. metal salts, and also from the expensive high boiling solvents used in obtaining them.

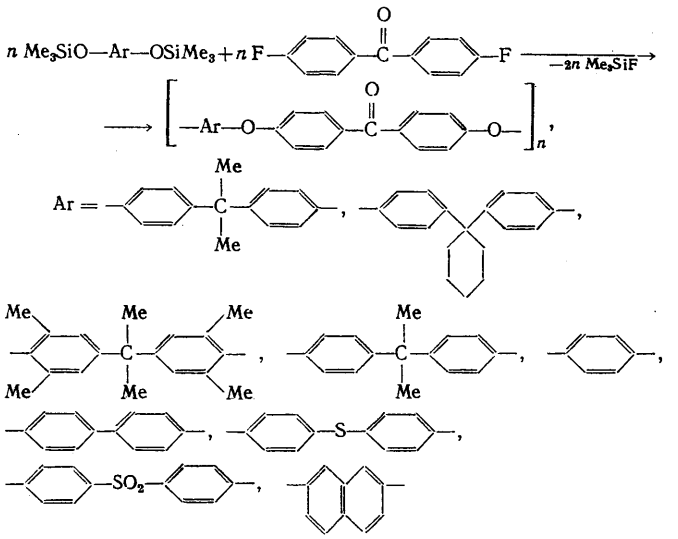
The use of silylated monomers enables polymers to be obtained which require no purification from large amounts of metal salts.

The reduction in reactivity of silylated bis-phenols requires the synthesis of polyesters to be conducted at elevated temperatures using catalysts such as KF and CsF.

The interaction of *O,O'*-trimethylsilyl-substituted bis-phenols with 4,4'-difluorodiphenylsulphone, which was carried out in bulk at temperatures up to 340 °C (Table 10), led to the preparation of poly(ether sulphones) with molecular weights reaching 17500.[16]

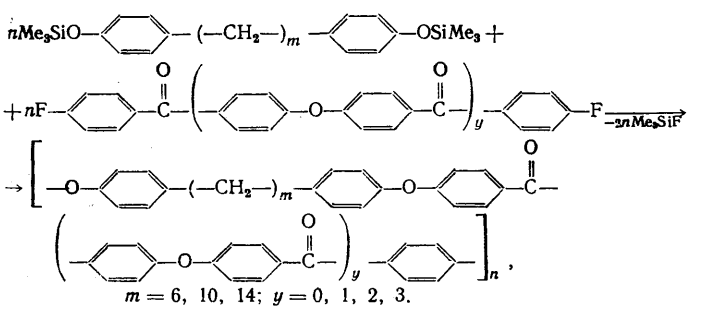


The reaction of *O,O'*-dimethylsilylated bis-phenols with 4,4'-difluorobenzophenone[17] leading to polyetherketones was effected under analogous conditions.



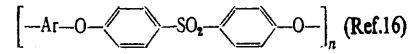
Some characteristics of the poly(ether ketones) obtained are shown in Table 11.

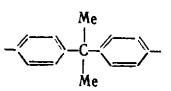
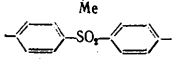
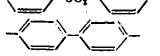
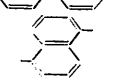
As continuation of these investigations the synthesis of fatty aromatic poly(ether ketones) with alternating aliphatic 'looseners' (spacers) and aromatic ether ketone blocks has been effected[73]



$m = 6, 10, 14; y = 0, 1, 2, 3.$

Table 10. Conditions for polycondensation of 4,4'-difluorodiphenylsulphone with *O,O'*-trimethylsilyl-substituted bis-phenols and some characteristics of the poly(ether sulphones) obtained of general formula



Ar	Polycondensation conditions		Yield, %	T_g, °C
	temperature, °C	time, h		
	180/320	0.5/2.5	98	185—195
	270/320/340	0.5/0.5/2.0	97	240—245
	250/320	0.5/2.5	95	240
	250/320	0.5/2.5	93	227

The poly(ether ketones) obtained in this way were crystalline substances, not forming mesophases.

2,6-Difluoropyridine is another activated difluoro-aromatic compound reacting with silylated bis-phenols[71]

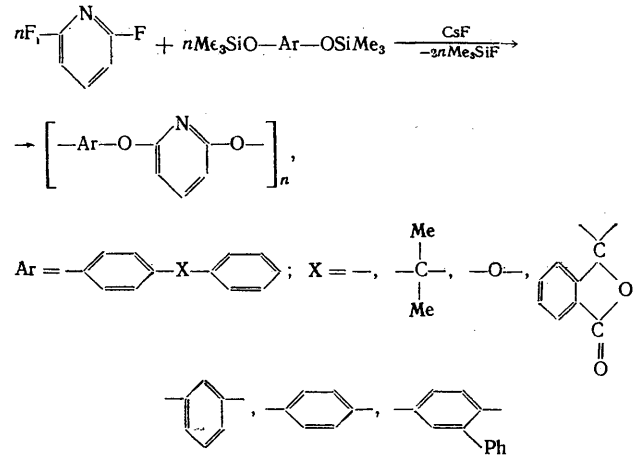
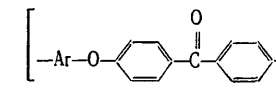
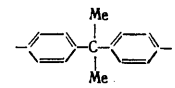
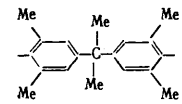
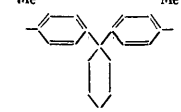
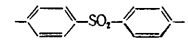
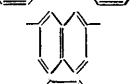
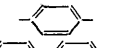
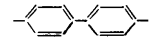


Table 11. Some characteristics of poly(ether ketones) of general formula



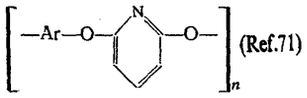
Ar	η^*_{rel}	$\overline{M}_n$**	$\overline{M}_w$***	T_g****, °C	Mp****, °C
	1.11	11 500	60 000	151—153	—
	1.06	1 700	3 200	143—145	—
	1.09	9 000	40 000	173—175	—
	1.46	7 000	—	184—186	—
	—	нр	нр	152—154	241—243
	2.21	—	—	—	343—345
	1.85	—	—	—	420—422

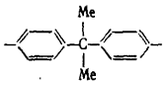
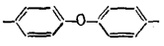
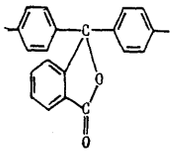
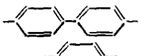
*Measured for 1% solutions in H_2SO_4 at 25 °C; **measured by osmometry in chloroform; ***measured by GLC in THF; ****determined by DSC at a temperature rise rate of 20° min^{-1}.

These processes are carried out in bulk at a maximum temperature of ~300 °C using CsF as catalyst by analogy to the synthesis of polyethers mentioned above (Table 12). As a result of

the low boiling point of 2,6-difluoropyridine (123 °C) a portion of it is removed from the reaction. Consequently the polycondensation processes were carried out with a small excess of 2,6-difluoropyridine (Table 12).

Table 12. Conditions of preparation and some characteristics of polyethers of general formula


(Ref.71)

Ar	Excess of 2,6-difluoro-pyridine, mol.	Yield, %	η_{inh}, dlitre g^{-1}
	0	99	0.25
	1.0	96	0.41
	3.0	96	0.47
	0	96	0.20
	1.0	97	0.42
	1.0	98	0.50
	0	91	0.45
	1.0	94	1.00
	—	96	1.40
	1.0	60	0.51

* Measured for solutions (c = 2 g litre^{-1}) in a mixture of dichloromethane–formic acid–trifluoroacetic acid (molar ratios 70:10:20) at 25 °C.

The conditions for carrying out the reaction of 2,6-difluoropyridine with silylated bis-phenols and the viscosity characteristics of the polyethers obtained are shown in Table 12.

As is seen from Table 12 the polyethers were obtained in almost all cases in yields exceeding 90% and with η_{inh} lying at 0.20–1.40 dlitre g^{-1}. The best viscosity characteristics were inherent in the film-forming polyether obtained from *O,O'*-disilylated phenylhydroquinone.

The molecular weight and thermal characteristics of the products of interaction of 2,6-difluoropyridine with silylated bis-phenols are shown in Table 13.

In addition to the homopolymeric polyesters the synthesis has been undertaken of copolymeric structures using an equimolar mixture of 2,6-difluoropyridine with 4,4'-difluorobenzophenone or 4,4'-difluorophenylsulphone as electrophilic comonomers[71]

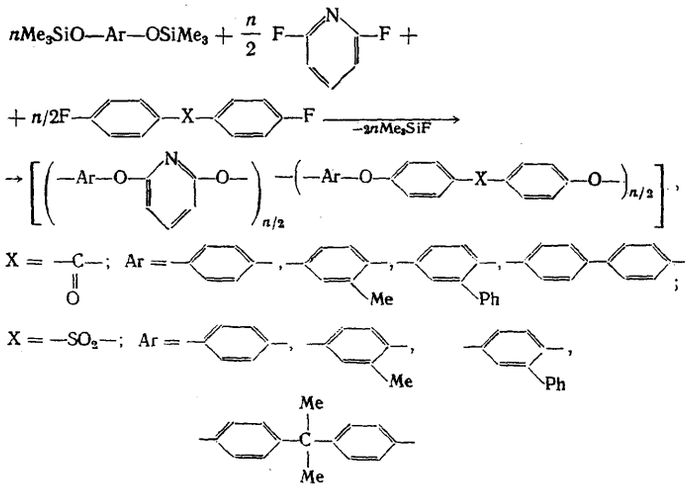
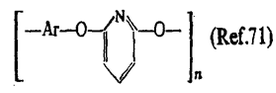
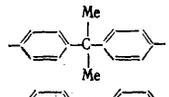
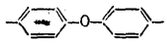
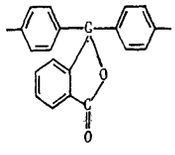
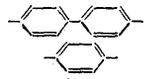
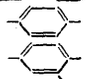


Table 13. Properties of polyethers of general formula


(Ref.71)

Ar	η^{*}_{inh}, dlitre g^{-1}	M_w 10^{-3} mol	T_g,** °C	M.p.**, °C	Temperature for mass loss °C, %		
					5	10	50
	0.133	95	108	—	442	462	520
	—	—	90	—	419	445	550
	0.128	—	195	—	458	469	570
	нр	—	119	253	430	458	620
	нр	—	100	272	360	430	555
	0.140	1200	71	—	425	451	485
	0.223	2900	116	—	445	460	560

* Measured for solutions in dichloromethane (c = 2 g litre^{-1}); ** date of DSC at heating rate 20° min^{-1}.

As follows from the data presented in Tables 14 and 15 polymers were obtained by copolycondensation possessing fairly high η_{inh} (0.44–1.56 dlitre g^{-1}) in combination with T_g lying within the limits 118–147 °C.

c) Synthesis of copolymers containing ether and ester groups

In addition to the synthesis of polyethers and polyesters the silylated monomers have been used for making high molecular compounds containing both ether and ester groups.[16] The reaction of di-methylsilylated *m*- and *p*-hydroxybenzoic acids with 4,4′-difluorodiphenylsulphone has been carried out for this purpose:[16]

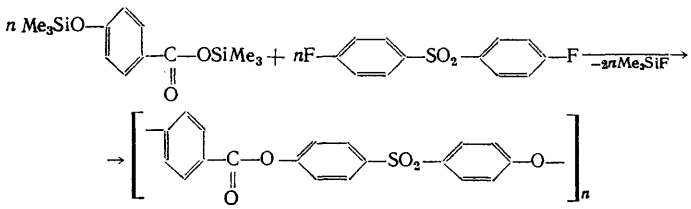
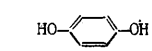
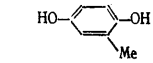
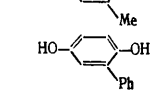
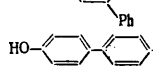
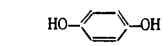
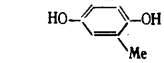
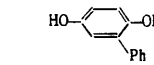
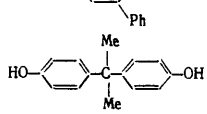


Table 14. Yields and some properties of copolymers obtained by thermal condensation of 2,6-difluoropyridine with 4,4′-difluorobenzophenone and silylated bis-phenols.[71]

bis-Trimethylsilylated bis-phenols	Yield, %	η^*_{inh}, dlitre g^{-1}	T_g, °C
	87	1.05	120**
	89	0.70	118
	97	0.44	123
	95	нр	128***

* Measured in a mixture of dichloromethane, formic and trifluoroacetic acids (70 : 10 : 20) c = 2 g litre^{-1} at 25 °C;
** after annealing at 180 °C for 1 h, m.p. = 278 °C;
*** m.p. = 293 °C.

Table 15. Yields and properties of polyethers obtained by block copolycondensation of 2,6-difluoropyridine with 4,4′-difluorodiphenylsulphone with various silylated bis-phenols.[71]

bis-Trimethylsilylated bis-phenol	Yield, %	η^*_{inh}, dlitre g^{-1}	T_g, °C
	85	0.47	131
	89	1.19	138
	94	1.55	147
	97	1.56	147

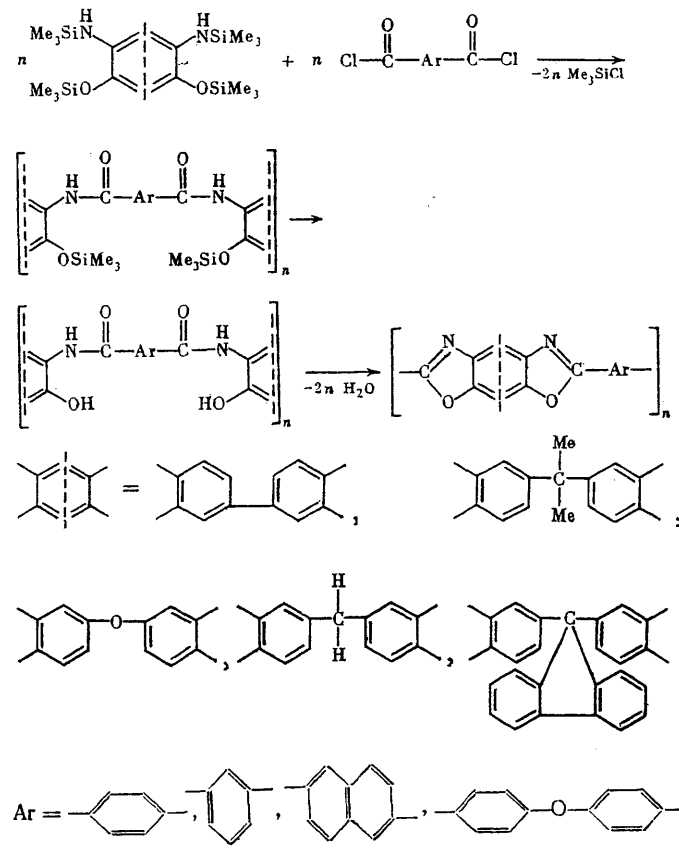
* Measured for solutions in mixtures of dichloromethane, formic and trifluoroacetic acids (70 : 10 : 20) at c = 2 g litre^{-1}.

The conditions for carrying out the polycondensation processes, yields and properties of the target copolymers are shown in Table 16.

It should be mentioned that attempts to involve activated dichloro aromatic compounds such as 4,4′-dichlorodiphenylsulphone and 4,4′-dichlorobenzophenone in reactions to obtain ester bonds proved unsuccessful. These compounds have too low a reactivity to undergo polycondensation reactions with phenolic groups rendered inert by silylation.

5. Polymers based on *N,O*-silylated aminophenols

The synthesis of polymers based on monomers containing silylated hydroxyl and amino groups is broadly represented by the synthesis of polybenzoxazoles using *N,N′,O,O′-tetrakis*-(trimethylsilyl)-bis-(*o*-aminophenols) and diacid chlorides of dicarboxylic acids.[20,22,79–81]

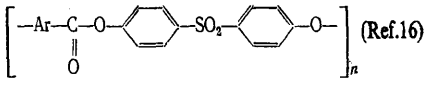


The synthesis of polybenzoxazoles based on silylated bis-(*o*-aminophenols) has been carried out by two-stage[20,79,81] and one-stage[80] methods. A detailed study of the two-stage process[20] and particularly of its first stage showed that, as in the synthesis of polyamides considered above, the use of silylated, rather than unsilylated, nucleophilic monomers led to the preparation of significantly higher molecular systems (Table 17).

The data given in Table 17 refer to poly-(*o*-hydroxy)amides devoid of silyl protection on the phenolic hydroxyls as a result of isolation from the reaction solution with methanol. Removal of silyl protection is necessary to increase the nucleophilic reactivity of the phenolic hydroxyl at the ring-closing stage. Polycyclodehydration of the poly-(*o*-hydroxy)amides thus obtained was carried out by heating at 250–260 °C in vacuum for 30 h. The polybenzoxazoles obtained

dissolved only in concentrated H_2SO_4. As a result their reprocessing into various materials such as films was effected at the stage of poly-(*o*-hydroxy)amides which are soluble in DMF, NMP, DMSO and pyridine. Some characteristics of polybenzoxazoles and films based on them are shown in Table 18.

Table 16. Conditions of carrying out block polycondensation of 4,4′-difluorodiphenylsulphone with disilylated hydroxybenzoic acids and some characteristics of the copolymers of general formula


(Ref.16)

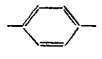
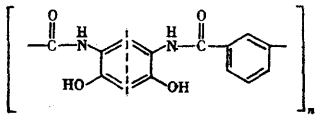
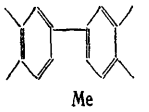
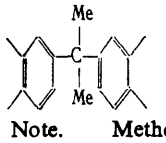
Ar	Reaction conditions		Yield, %	T_p, °C
	temperature, °C	time, h		
	250/320	0.5/2.5	91	137
	250/320	0.5/2.5	96	215

Table 17. Comparison of η_{inh} of poly-(*o*-hydroxyamides) from bis-(*o*-aminophenols) and their silylated derivatives

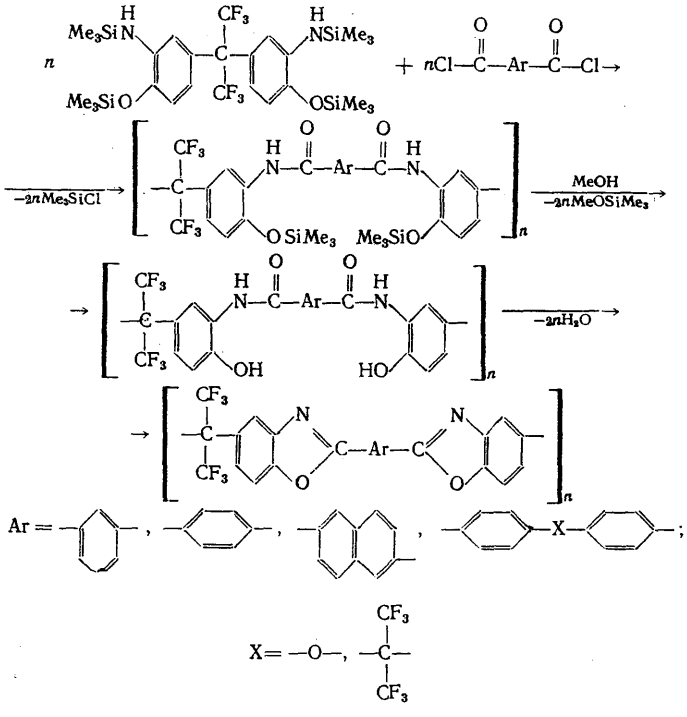

(Ref.20)

	Method A	Method B
	0.33	0.50
	0.16	0.55

Note. Method A was polycondensation using unsilylated bis-(*o*-aminophenol); method B was polycondensation using silylated bis-(*o*-aminophenol); polycondensation was carried out by reaction of bis-(*o*-aminophenol) (2.5 mmole) with isophthaloyl chloride (2.5 mmole) in DMA (5 ml) at 0–5 °C for 8 h in a stream of N_2; all polymers were obtained in quantitative yield; viscosities were measured in DMA at 30 °C and c = 0.5 g dlitre^{-1}.

The most interesting synthesis of polybenzoxazoles from silylated monomers is that based on weakly basic bis-*o*-aminophenols. One of such monomers is 2,2-bis-(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane. Further interest in the polymer based on it arises because aromatic polycondensates containing the hexafluoroisopropylidene group are characterised by a combination of enhanced solubility and good thermal characteristics.[82]

A detailed study of hexafluoroisopropylidine-containing polybenzoxazoles obtained according to:



showed that silylation of 2,2-bis-(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane led to an increase in the nucleophilic reactivity of this monomer.[20] Thus η_{inh} was equal to 0.08 dlitre g^{-1} for the polyisophthalamide based on the unsilylated monomer but η_{inh} was 0.64 dlitre g^{-1} for the poly-(*o*-hydroxy)amide based on the silylated monomer and synthesised under the same conditions.

Introduction of the hexafluoroisopropylidene grouping imparted increased solubility not only for the poly-(*o*-hydroxy)amide but also for the polybenzoxazole in full agreement with the previous report (Table 19).[82]

Viscosity and thermal characteristics of the hexafluoroisopropylidene-containing polybenzoxazoles and some strength characteristics of films based on them are shown in Table 20.

The thermal characteristics of hexafluoroisopropylidine-containing polybenzoxazoles shown in Table 20 surpass in some degree the corresponding characteristics of analogous systems obtained by reductive polyheterocyclisation.[5,6,83,84] This is in agreement with existing ideas[85] on the influence of the method of synthesis of polybenzazoles on their properties.

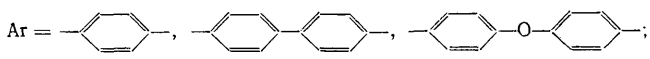
The low strength characteristics of films obtained from hexafluoroisopropylidene-containing polybenzoxazoles (Table 20) are somewhat surprising. Nonetheless these polymers are considered to be very promising thermostable polymeric materials.[20]

6. Polymers based on *S*-silylated dithiols

In spite of the fact that the reactivity of *S*-trialkylsilylated thiols is close to the reactivity of *N*-silylated amines, reactions of compounds containing an Si–S bond have been paid insignificant attention by

investigators. Nonetheless the reaction of *S*-silylated aromatic dithiols with activated dihalo aromatic compounds has been carried out:[18]

$$n\mathrm{Me_3Si{-}S{-}Ar{-}S{-}SiMe_3} + n\mathrm{X{-}Ar'{-}X} \xrightarrow[-2n\mathrm{Me_3SiX}]{} \mathrm{[{-}S{-}Ar{-}S{-}Ar'{-}]}_n,$$

Ar =  ;

X = F, Cl;

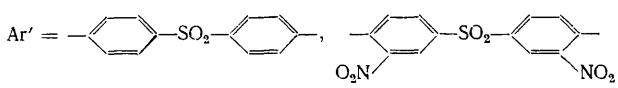
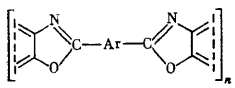
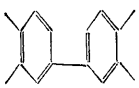
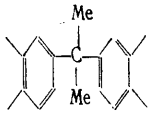
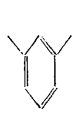
Ar′ = 

Table 18. Some characteristics of polybenzoxazoles of general formula



and polybenzoxazole films.[20]

	Ar	T_g^*, °C	T_{dec}^{**}, °C		Properties of films	
			in air	in N_2	σ_s, kg.cm^{-2}	ε_{rel}, %
		290	570	620	1980	7
		240	500	530	530	2

* Determined by thermomechanical analysis at a heating rate of 10° min^{-1} in air;

** temperature for loss of 10% initial weight (TGA, heating rate 10° min^{-1}).

The properties of the polysulphides obtained are shown in Table 21. As is seen from Table 21 aromatic polysulphides with moderate η_{inh} (0.6–0.7 dlitre g^{-1}) were obtained from the reaction (HMPA, 50 °C) of *S*-silylated dithiols with bis-(4-chloro-3-nitrophenyl)sulphone. Bis-(4-fluorophenyl)sulphone possesses little reactivity. Its reaction in solution with *S*-silylated dithiols was effected in TMS at 220 °C using CsF as catalyst. The polysulphides obtained possessed η_{inh} close to 0.3 dlitre g^{-1}.

Summing up all the above mentioned results on polycondensation and polyaddition reactions using silylated nucleophiles[10] it should be noted that:

1) silylation of nucleophilic monomers leads to compounds which are easy to purify, in particular, silylated products may be purified by distillation;

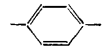
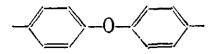
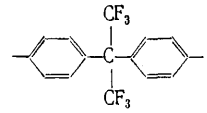
2) the majority of silylated monomers are readily soluble in organic solvents which facilitates polycondensation and polyaddition reactions in various reaction media, from low to high boiling and/or polar solvents;

3) polycondensation processes using silylated monomers may be carried out in neutral media with separation of neutral compounds as byproducts, particularly chlorotrimethylsilane, which may be used once again to obtain silylated monomers;

4) in several cases silylation of nucleophilic monomers leads to an increase in reactivity which makes it possible to carry out the synthesis of polymers under milder conditions and at higher rates. In individual cases silylation is an effective route to involve unreactive compounds in polymer synthesis;

5) the silylation of multifunctional monomers used in polyheterocyclisation reactions may lead to an increase in the difference in reactivity of neighbouring reaction centres thus enabling a smoother course for selective polyacylation.

Table 19. Solubility of hexafluoroisopropylidene-containing poly-(*o*-hydroxy)amides and polybenzoxazoles.[20]

Ar	Solubility of poly-(*o*-hydroxy)amide / Solubility of polybenzoxazole						
	NMP	DMSO	DMF	PhN	THF	Me_2CO	*o*-chloro-phenol
	++ / −	++ / −	++ / −	++ / −	++ / −	++ / −	+ / +
	++ / −	++ / −	++ / −	+ / −	− / −	− / −	− / −
	++ / −	++ / −	++ / −	++ / −	++ / −	+ / −	− / −
	++ / +	++ / −	++ / −	++ / +	++ / −	+ / −	+ / ++
	++ / ++	++ / ++	++ / ++	++ / ++	++ / −	++ / −	+ / ++

Note. (++) denotes soluble at room temperature; (+) partially soluble or swells; (–) insoluble.

The discussed merits of reactions using silylated monomers have swung the interest of investigators towards polycondensation reactions in the presence of silylated agents.

III. Polycondensation reactions in the presence of silylating agents

Since the synthesis of polymers using silylated monomers requires previous synthesis and purification of the latter a simpler way of obtaining polymers would be their synthesis in the presence of

silylating agents. Thus on reacting 3,8-diaminophenanthridine with terephthaloyl chloride in a mixture of NMP and HMPA at 0 °C in the presence of chlorotrimethylsilane, a higher molecular polyamide was obtained than in the presence of such widely used additives as LiCl and $CaCl_2$ (Table 22).

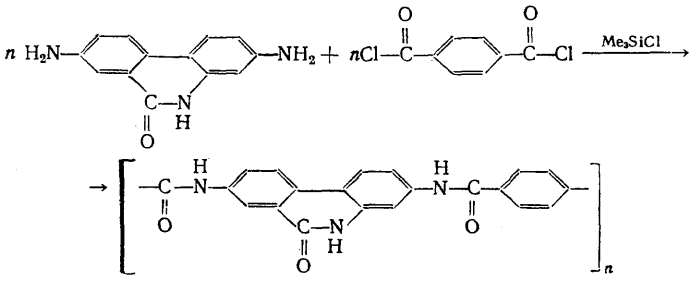
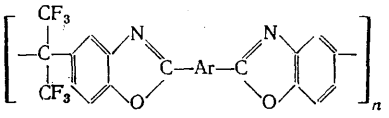
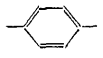
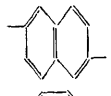
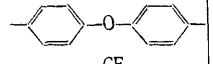
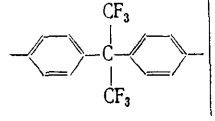


Table 20. Some characteristics of polybenzoxazoles of general formula



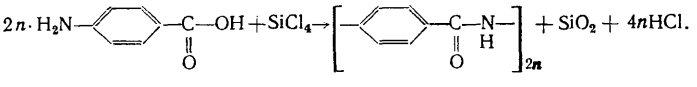
and films based on them.[20]

Ar	η_{inh}, dlitre g^{-1} (H_2SO_4, 30 °C)	T_g^*, °C	T_{dec}, °C		Properties of films	
			in air	in N_2	σ_s, kg.cm^{-2}	ε_{rel}, %
	—	260	530	545	—	—
	—	310	545	555	—	—
	0.76	325	540	560	930	6
	0.49	300	525	530	430	2
	0.46	295	545	555	680	3

Determined by thermomechanical analysis at a heating rate of 10° min^{-1} in air.

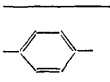
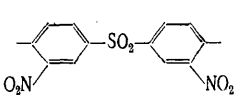
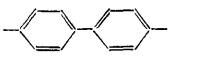
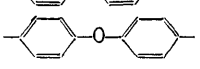
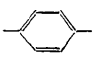
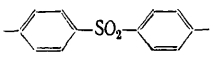
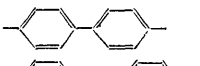
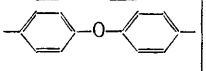
A similar approach to obtaining high molecular polyamides has been used in copolymer synthesis.[87]

Another example of carrying out a polycondensation in the presence of a silylating agent is the homocondensation of *p*-aminobenzoic acid in pyridine in the presence of $SiCl_4$.



Tetrachlorosilane has also been used as silylating agent in the reaction of *p*-phenylenediamine with terephthalic acid and of *m*-phenylenediamine with isophthalic acid.[88] The results of these processes, belonging to a variety of 'direct' polycondensation,[1,2] are shown in Table 23.

Table 21. Conditions of synthesis and viscosity characteristics of aromatic polysulphides of general formula $[-S-Ar-S-Ar'-]_n$.[18]

Ar	Ar'	Synthesis conditions			η_{inh}**, dlitre g^{-1}
		solvent	T, °C	time, h	
		HMPA	50	24	0.64
	»	ditto	50	24	0.67
	»	ditto	50	24	0.76
		TMS	220	24	0.29
	»	ditto	220	24	0.30
	»	ditto	20	24	0.30

*Solvents for polycondensation: HMPA is hexamethylphosphoramide, TMS tetramethylenesulphone; **η_{inh} was measured in HMPA at 30 °C.

Table 22. Influence of LiCl, $CaCl_2$ and Me_3SiCl in solvents on η_{inh} of poly-3,8-phenanthridinonediylterephthalamide.[86]

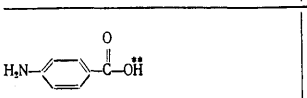
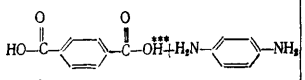
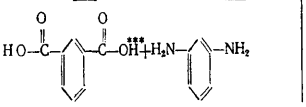
Solvent	LiCl				Me_3SiCl			$CaCl_2$
	1*	2	3	4,5	1	2	3	1
HMPA–NMP (1:1)	3.71	3.74	3.79	—	6.13	6.68	—	—
NMP–DMA (1:1)	0.83	2.62	3.91	4.01	0.74	—	1.84	4.48

*1 mole LiCl per mole diamine, etc.

As follows from the data shown in Table 23 an oligomer is obtained in 41% yield when a stoichiometric amount of $SiCl_4$ is used. On using a 20% excess of $SiCl_4$ the polyamide was obtained in quantitative yield and its molecular weight was 13 400. Polyamides with lower molecular weight characteristics were

obtained on reacting *p*-phenylenediamine with terephthalic acid. This is evidently linked with the low solubility of terephthalic acid in the reaction medium.

Table 23. Conditions of synthesis of aromatic polyamides in the presence of $SiCl_4$.[88]

Monomers	Molar ratio $SiCl_4$: :monomer	[Monomer], mol.litre^{-1}	Yield, %	[η]*, dlitre g^{-1}	M_n
	0.50 0.62 0.63	0.74 0.67 1.00	41 96 99	0.31 1.43 1.97	— 1 100 13 400
	0.80	0.56	94	0.60	5 300
	0.62	0.66	98	0.51	—

Note. Polycondensation was carried out at 0 °C for 24 h.

*Measured in H_2SO_4 at 30 °C; **solvent pyridine; *** solvent chlorobenzene : pyridine (2 : 1).

An interesting aspect of this synthetic method is the formation of filler materials in the reaction process. SiO_2 is formed as a result of the polycondensation.

— o0o —

It has been shown that the silylation method, particularly processes using *N*-silylated diamines, is an easy and promising route for the synthesis of high molecular condensation polymers. New polycondensation reactions using silylated monomers are at the development stage at the present time. However, in the main this area continues to remain little studied. The most characteristic distinguishing feature of the silylation method is the fact that silylated nucleophilic monomers differ markedly in reactivity from the initial nucleophiles. This method may therefore find new regions of application for making new condensation polymers and for developing new synthetic routes for obtaining various known polymers.

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Aromatisation of low-molecular-weight paraffins on pentasil group zeolites

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ABSTRACT. Experimental data on the application of pentasil group zeolites in the aromatisation of low-molecular-weight paraffins are surveyed. Modern ideas concerning the mechanism of the aromatisation and the nature of the active centres in pentasil are examined. Examples of the application of pentasil-containing catalysts in technological processing of gaseous hydrocarbons are presented.

The bibliography includes 235 references.

Contents

I. Introduction 885
II. Structure and active centres of pentasils 886
III. Aromatisation of low-molecular-weight paraffins 888
IV. Application of pentasil-based catalysts in technological processes for the preparation of valuable chemical products from hydrocarbon gases 900

I. Introduction

Low-molecular-weight hydrocarbons are a readily available and cheap raw material for the synthesis of polymeric materials, high-octane components of motor fuel (C_6-C_8 isoalkanes and aromatic hydrocarbons), as well as various intermediates in fine organic synthesis.[1–3] Among the principal sources of lower paraffins, one should distinguish in the first place the byproduct petroleum gas (C_2-C_5 alkane content up to 70%) and natural gas (overall content of ethane, propane, and butanes up to 25%),[4,5] the scale of the extraction of which runs into tens and hundreds of billions of cubic metres per year respectively. A tendency has arisen recently towards a more complete utilisation of petroleum by processing also its heavy fractions and towards an increase of the output of apparatus for thermal and catalytic cracking—the principal degradative processes used in modern petrochemical and petroleum processing industry. This has resulted in a considerable increase in the evolution of waste gases in which C_2-C_4 paraffins predominate and which contain an appreciable amount of the corresponding alkenes. The processes based on CO and H_2—the gaseous coal processing products—also occupy a fairly important place in the manufacture of lower hydrocarbons.[6,7] Until recently, a considerable proportion of the components of natural, byproduct, and petroleum industrial gases have been used merely as industrial fuels and have not found applications in the synthesis of chemical products.

The task involving the effective utilisation of hydrocarbon gases has stimulated the search for new catalysts, among which synthetic zeolites occupy a special place.[8,9] The first generation zeolites (faujasites, mordenite, erionite, etc.) are replacing traditional catalysts based on amorphous aluminosilicates in petroleum cracking processes, in the alkylation of paraffins and aromatic hydrocarbons, and in the oligomerisation of lower alkenes. A new stage in the development of zeolite catalysis involves the synthesis of high-silica pentasil group zeolites.[1–3,10] Zeolites of this structural type, which have no natural analogues, were first synthesised by the Mobil Oil Company at the beginning of the 1970's. They were given the abbreviated designations ZSM-5 and ZSM-11.[11–17] In the Soviet Union, analogues of these zeolites are referred to as pentasils of the TsVK and TsVM types and ultrasil.[15] New methods of synthesis of pentasils, in the lattices of which aluminium atoms have been replaced by boron, iron, gallium, germanium, zinc, and chromium atoms as well as atoms of other elements, have been developed recently.[18–20]

Pentasil-based catalysts have found applications in many large-scale petroleum processes such as isomerisation, disproportionation, and alkylation of aromatic hydrocarbons,[21–23] the cracking of gas oil fractions,[3,24] deparaffinisation of petroleum fractions,[24] the conversion of methanol into hydrocarbons,[25–27] etc. In these processes, pentasils proved to be more effective as selective catalysts than the previously employed first generation zeolites or non-zeolitic systems of various compositions. In addition, pentasils possess the unique ability to convert lower paraffins and alkenes into higher-molecular-weight products.[3,27–32] C_2-C_4 alkenes are almost quantitatively converted into high-octane components of motor fuel on pentasils at atmospheric pressure and at temperatures in the range 300–350 °C.[11–13,28–30] During the last 4–5 years, there has been a growth of interest in pentasils as catalysts of the aromatisation of lower paraffins. The modification of pentasils by the addition of various transition elements made it possible to obtain catalytic systems for the conversion of propane and butanes into C_6-C_{10} aromatic hydrocarbons with a selectivity of 60–70%.[31–34]

The results of the study of the catalytic properties of zeolites, including pentasils, in various reactions have been treated systematically in a number of reviews[1–3,16,22–27,35,36] published at the beginning of the 1980's. The aim of the present review is to survey and analyse the information accumulated during the last 5–6 years about the reactions of low-molecular-weight paraffins in the presence of pentasils of various compositions, to discuss the possible mechanisms of these reactions, and to consider certain technological aspects of the use of pentasil-based catalysts in the processing of hydrocarbon gases.

II. Structure and active centres of pentasils

The skeleton of zeolites—crystalline aluminosilicates—consists of aluminium–oxygen and silicon–oxygen tetrahedra, which have common vertices and form the structural elements of the lattice—tetrahedral and hexahedral prisms, cancrinite and sodalite cells, cubooctahedra, etc.[37,38] Without going into details, which have been described in a number of reviews and monographs,[8,9,16,37,38] we shall note only the principal features of the structure of pentasils. The pentasil skeleton is based on five-membered rings formed predominantly by silicon–oxygen tetrahedra, since the concentration of aluminium in these zeolites is low (not more than 5 atoms per unit cell, which corresponds to the ratio Si/Al ranging from about fifteen to tens of thousands).[3,14,38] The five-membered rings are joined up into cells consisting of eight such rings and form chains which are combined into layers, each chain in the layer representing the mirror image of the neighbouring chain (Fig. 1). In the skeleton of pentasils of type ZSM-5 and ZSM-11 there exists a system of pores consisting of channels intersecting at right angles, which are produced by ten-membered rings. The porous structure of the ZSM-5 zeolite includes both straight (0.54 × 0.56 nm) channels with an elliptical cross-section and sinusoidal (0.51 × 0.55 nm) channels with a circular cross-section. The pore system of the ZSM-11 pentasil consists of straight channels with an elliptical cross-section.

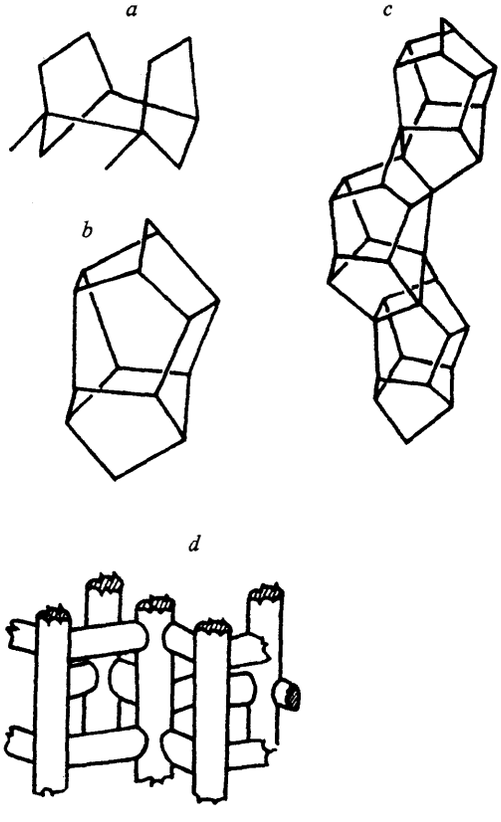
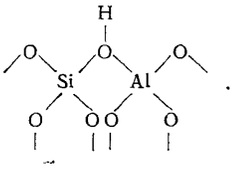
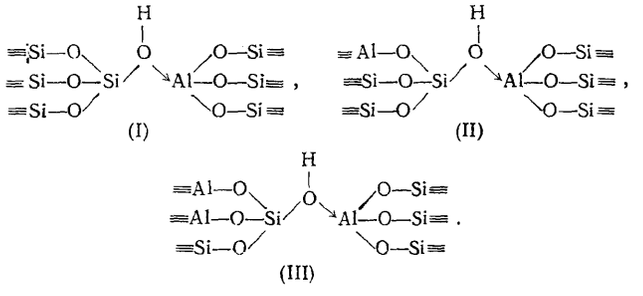


Figure 1. The structure of pentasil: *a*, structural element; *b*, cell made up of eight five-membered rings; *c*, chain made up of cells; *d*, schematic representation of the channel structure of pentasil.[3]

It must be emphasised that the aluminium atoms occupy a special position in the crystal lattice of zeolites. They substitute isomorphously the silicon atoms in the structural skeleton but are involved in tetrahedral coordination with respect to oxygen atoms. As a result of this, the coordination number and valence of aluminium are not the same, which leads to the appearance of an excess negative charge on the aluminium–oxygen tetrahedron AlO_4^-. This charge may be compensated either by a metal cation or by a proton (in the decationated forms of the zeolite). The compensating proton forms a covalent bond with one of the four oxygen atoms in the AlO_4^- tetrahedron, which creates isolated structural hydroxy-groups of the bridging type:



An IR spectroscopic study of the interaction of the OH bridging groups with the molecules of adsorbed bases[39–49] established that they are strong Brønsted acid centres (B-centres). According to modern ideas[42,47–52] based on quantum-chemical calculations and experimental IR data, the entire wide variety of the acid hydroxy-groups reduces to three principal types with different numbers of aluminium atoms in the immediate structural environment of the hydroxyl.



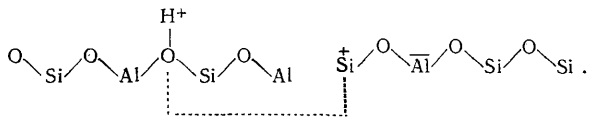
The acid properties of the hydroxyls are weakened on passing from (I) to (III) and further to silanol groups Si–OH, which have no proton-donating capacity. High-silica pentasils and mordenites contain type (I) OH groups and terminal silanol hydroxyls similar to the surface hydroxy-groups on silica gel.[46,49,50] Apart from the isolated bridging hydroxyls, pentasils include bridging OH groups forming fairly strong hydrogen bonds with the lattice oxygen atoms.[46,53] The concentration of such hydroxyls can reach 20% of the total number of OH groups.[46] According to Medin et al.,[53] these groups have unusual properties. For example, at room temperature they are capable of interacting with adsorbed paraffin molecules, while at elevated temperatures they undergo a transition to an isolated state. According to quantum-chemical calculations,[54] hydroxyls of this type should have stronger electron-donating properties than isolated bridging OH groups.

Apart from B-centres, zeolites contain aprotic (Lewis) acid centres (L-centres) possessing electron-accepting properties. Various coordinatively unsaturated lattice atoms or ions having an unoccupied *p* orbital as well as exchange cations with a positive charge constitute the zeolite L-centres. In the structure of dehydroxylated hydrogen-forms of zeolites, AlO_4^- tetrahedra lacking

a proton compensating their charge and having the properties of a Lewis base, are also present.

The results of IR spectroscopic studies[46–53] have shown that, on dehydroxylation of decationated pentasils and mordenites obtained by direct hydrothermal synthesis, aprotic acid centres of three types are formed: one of them consists of coordinatively unsaturated lattice aluminium atoms, others consist of silicon ions, and finally the third group comprises aluminium atoms outside the lattice. In the dealuminated mordenites, L-centres of only one type—tricoordinate lattice silicon ions—are formed after the removal of OH groups.

According to the results of a number of studies,[17,55,56] high-silica zeolites of the type of pentasil and mordenite contain also a smaller amount of very acid ("superacid") centres. These are protic centres whose acidity has been enhanced as a result of the inductive effect of a neighbouring Lewis centre.[57]



Thus acid centres of different nature have been identified in zeolites by the IR spectroscopy of adsorbed molecules. The ratio of the concentrations of the L- and B-centres depends on the structure of the zeolite, the composition of the skeleton, the thermal stability of the hydroxyl coating, and the chemical nature of the substances used to modify the inner and outer surfaces of the catalyst.[8,9,34]

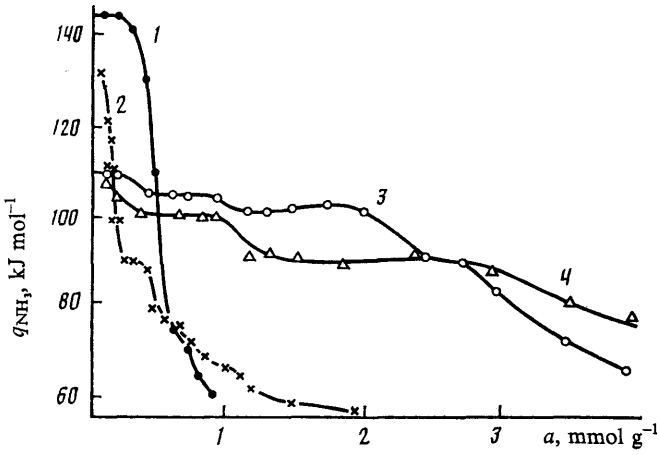


Figure 2. Differential heats of adsorption of ammonia on zeolites at 30 °C:[59] *1*, dealuminated mordenite with Si/Al = 24; *2*, pentasil of the type H-TsVK with Si/Al = 40; *3*, HNaY (degree of decationation α = 80%); *4*, HNaX (degree of decationation α = 80%).

Apart from IR spectroscopy, adsorption microcalorimetry,[40,58–66] heterophase isotope exchange between deuterium and hydroxy-groups,[67–71] programmed thermal desorption of ammonia and organic nitrogen-containing bases,[72,73] etc. have been used to investigate the acidity of zeolites of different structure, including pentasils. Adsorption microcalorimetry, based on the direct measurement of the differential heats of adsorption of nitrogen-containing bases and especially of ammonia, is most suitable for the quantitative estimation of the concentration and strength of the acid centres. The stepwise character of the curves reflecting the dependence of the differential heat of adsorption of ammonia q_{NH_3} on the amount of adsorbed ammonia Q shows that the inhomogeneity of the adsorption centres of zeolites is discrete in nature (Fig. 2). The acidity spectra of certain zeolites having different compositions and structures (Fig. 3) contain bands with the same q_{NH_3}. These indicate the presence of centres of identical strength in different zeolites but at different concentrations. With increase in Si/Al, a trend is observed towards an increase in the strength of the acid centres and a decrease in their number.[63–66] Comparison of the acidity spectra has shown that both pentasils and mordenites contain strong acid centres with $q_{NH_3} > 120$ kJ mol^{-1}.[61–63] However, in contrast to mordenites, pentasils contain no centres adsorbing ammonia with $q_{NH_3} > 130$ kJ mol^{-1}.

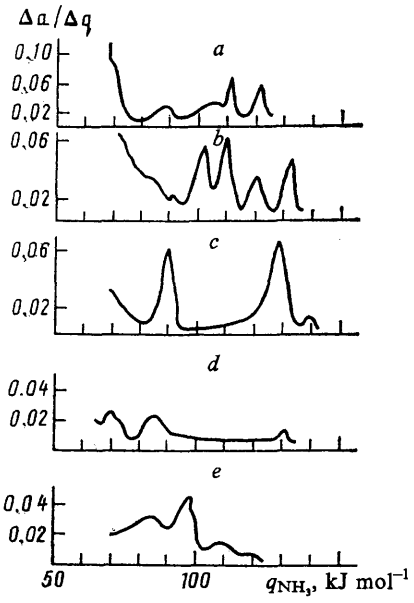
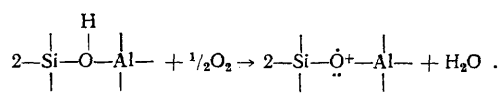


Figure 3. Distribution of acid centres of different structure with respect to energy:[63] *a*, zeolite L (α = 82%); *b*, mordenite (α = 90%); *c*, dealuminated mordenite with Si/Al = 9; *d*, pentasil of type H-TsVK with Si/Al = 30; *e*, pentasil of type H-TsVM with Si/Al = 20 ($\Delta a/\Delta q$ = fraction of acid centres with a specific q_{NH_3}).

The acid centres of pentasils are distinguished by a high thermal stability. The results of measurements of the concentration of hydroxy-groups by heterophase isotope exchange and adsorption microcalorimetric methods[63,71] showed that the protic centres of pentasils begin to decompose above 700 °C and that, even after heat treatment at 800 °C, about 40% of the hydroxyls persist on the surface. Pentasil vacuum heat-treated at 800 °C contains strong acid centres which adsorb ammonia with q_{NH_3} = 110–130 kJ mol^{-1}.[63] The number of these centres is approximately three times smaller than for the specimen heated at 500 °C.

Together with acid centres of different nature, the zeolites contain oxidation-reduction centres, which were identified by the EPR method.[74] The Brønsted acid centres of pentasils can be converted into centres of another type—solid state defects—as a result of high-temperature heat treatment (> 500 °C):[75]



When these centres interact with ionisable organic molecules, radical-cations can be produced.

III. Aromatisation of low-molecular-weight paraffins

The first communications about the catalytic conversion of low-molecular-weight paraffins into aromatic hydrocarbons appeared at the beginning of the 1970's.[76–79] According to thermodynamic calculations,[79] at 627 °C the equilibrium constant of the reaction $3C_2H_6 \rightleftarrows C_6H_6 + 6H_2$ is ~21, which corresponds to 78% of benzene in the equilibrium mixture at atmospheric pressure. The equilibrium constant of the reaction 2 iso-$C_4H_{10} \rightleftarrows C_6H_4(CH_3)_2 + 5H_2$ is 16.2 at 427 °C and 1.2×10^4 at 527 °C.[76] Table 1 presents the calculated temperatures at which the free energies ($\Delta G°$) of the alkane aromatisation and dehydrogenation reactions become zero. The conversion of ethane, propane, and hexane into benzene requires much lower temperatures than their dehydrogenation.[80]

Table 1. Temperature (°C) at which benzene and olefins are formed from various alkanes with $\Delta G° = 0$.[80]

Alkane	Benzene	Alkenes
Methane	1075	1350 (C_2H_4)
Ethane	575	774 (C_2H_4)
Propane	450	655 (C_3H_6)
n-Hexane	320	575 (C_6H_{12})*

*2-Methylpentene.

By analogy with the dehydrocyclisation of paraffins containing six and more carbon atoms, bifunctional deposited metallic reforming catalysts, which exhibit a dehydrogenating activity, were used initially for the conversion of light alkanes.[76–79,81–89]

Ethane may be aromatised in the presence of an M/Al_2O_3 catalyst, where M = Pt, Pd, Ru, Rh, or Ir.[79,81–83] Aluminoplatinum catalysts exhibited an appreciable activity in the aromatisation reactions of propane,[77,84,85] butanes,[76,86] and pentane.[77] Aromatic hydrocarbons have also been obtained from n-butane in the presence of Mo, W, Cr, V, and Mn oxides deposited on Al_2O_3.[78] The aromatisation reactions of lower paraffins on non-zeolitic catalysts have been examined in detail in a number of reviews.[87–89] We may note that, in the presence of the M/Al_2O_3 catalysts the selectivity in the formation of aromatic hydrocarbons S_{arom}, defined as the ratio of the yield of the aromatisation products to the overall degree of conversion, does not exceed 20%. Most of the initial hydrocarbon is converted into cracking and condensation products. As a result of the deposition of these products on the surface, the activity of the catalyst falls rapidly during the reaction.

A new stage in the study of the conversion of lower paraffins with less than six carbon atoms into aromatic hydrocarbons is associated with the use of zeolites of the pentasil group. In the decationated form, these zeolites are capable of aromatising saturated hydrocarbons even in the absence of dehydrogenating components. Modification of pentasils by various metals made it possible to increase significantly the degree of conversion of paraffins and S_{arom}.

All the promoting elements can be divided arbitrarily into two groups. The first includes noble metals (Pt, Rh, Pd), which increase the degree of conversion and the yield of aromatic hydrocarbons, while the second group includes certain Group II and III elements (Zn, Cd, Ga), in the presence of which S_{arom} increases sharply. Examples of the aromatisation of C_2-C_5 paraffins in the presence of pentasils in the hydrogen-form and modified catalysts are examined below.

1. Decationated pentasils

Pentasils of the type H-TsVM exhibit an appreciable activity in the aromatisation of ethane.[90–96] At 600 °C and for a contact time $\tau \simeq 30$ s, the yield of aromatic hydrocarbons relative to the paraffin passed through the system ($A_{C_2H_6}$) was 10% on a specimen Si/Al = 18. Under the same conditions, the degree of conversion of propane was appreciably higher. In the range 500–600 °C, the degree of conversion of propane ($x_{C_3H_8}$) varied from 72 to 98%, while $A_{C_3H_8}$ varied from 14 to 37%. At $T \geqslant 600$ °C and for $\tau \geqslant 20$ s, propane undergoes a thermal transformation: $x_{C_3H_8} = 40-80\%$.[97,98] In the presence of a pentasil of the type of ultrasil with Si/Al = 22 for $x_{C_3H_8} = 93\%$ and $A_{C_3H_8} = 24\%$ (600 °C, $\tau = 30$ s), most of the propane was converted into methane (37%), ethane (21%), and C_2-C_4 alkenes (14%).[99,100] On silicalite containing less than 0.03 wt.% Al, the main reaction pathway at 630 °C and for $\tau \simeq 5$ s was the formation of C_1-C_3 hydrocarbons (88%), while $A_{C_3H_8}$ did not exceed 3%.[101] On type H-TsVK pentasil (Si/Al = 30), at 600 °C and for $\tau = 8$ s, $S_{arom} \simeq 10\%$ for $x_{C_3H_8} = 67\%$.[102] Under these conditions, ethane was not converted into aromatic hydrocarbons, while in the reaction with isobutane A reached 23%.

The aromatisation of propane has also been studied under relatively mild conditions (500–550 °C, $\tau \leqslant 10$ s, $p_{C_3H_8} = 0.01-0.1$ MPa) where the contribution of the thermal process is insignificant.[101–104] The liquid catalytic reaction mixture consisted, as at 600 °C, only of aromatic hydrocarbons, among which benzene, toluene, and xylenes predominated. Despite the fact that the reaction conditions and the compositions of the catalyst in a number of studies were different,[101–103] S_{arom} and the proportions of the aromatic C_6-C_8 hydrocarbons at 500–550 °C proved to be almost identical: 25–30% of benzene, 46–50% of toluene, and 20–26% of xylenes plus ethylbenzene with $S_{arom} = 25-30\%$. Only in some instances[104,105] did S_{arom} reach ~50% at 500–650 °C.

Apart from temperature and contact time, an important factor influencing the degree and nature of the transformation of lower paraffins in the presence of pentasils is the ratio of the concentrations of silicon and aluminium in their lattices. The role of the composition of the skeleton of decationated pentasils in the aromatisation of propane and isobutane has been studied.[100,106–111]

An increase in the Si/Al ratio in ultrasils from 22 to 95 led to a decrease in $x_{C_3H_8}$ from almost 100 to 42% (at 600 °C and for $\tau \simeq 30$ s).[106] Simultaneously with the falling degree of conversion, the activity of the catalyst fell in the aromatisation, cracking, and coke formation reactions and to a lesser extent in the dehydrogenation of propane.[100]

The activity of pentasils of type H-TsVK and H-TsVM with Si/Al = 15–140 in the transformations of propane and isobutane[108–110] also increased appreciably with increase in the content of aluminium [Al] in the skeleton (Fig. 4). The quantity $x_{C_3H_8}$, which increases monotonically with increase in [Al], reaches ~80% at 600 °C and for $V = 450$ h^{-1} on specimens with Si/Al = 15–24. The dependence of $A_{C_3H_8}$ on the composition of pentasils has a somewhat different character (Fig. 4, curve *2*). The plot shows clearly two sections, one of which corresponds to the variation of A with increase in [Al] from 0.3 to 1.4 wt.% and the other corresponds to the variation of A as [Al] increases from 1.4 to 3.2 wt.%. On zeolites containing ≤1.4 wt.% Al, $A_{C_3H_8}$ ranges from 5 to 8%, which is almost identical with the yield of aromatic hydrocarbons on quartz, i.e. under the conditions of the thermal conversion of propane. The aromatisation of the more reactive isobutane does not require as much Al in the skeleton as for the transformation of propane,[109] but the maximum value of $A_{C_4H_{10}}$ (42% at 600 °C and for $V = 450$ h^{-1}) was obtained on the catalyst with Si/Al = 20.

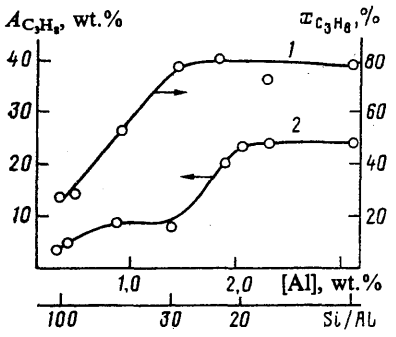


Figure 4. Dependence of the degree of conversion of propane (curve *1*) and of the yield of aromatic hydrocarbons at 600 °C (curve *2*) on the aluminium concentration in the pentasil skeletons.[109]

The composition of the skeleton influences significantly not only the activity of pentasils but also the selectivity of their action. Fig. 5 presents the dependence of $A_{C_3H_8}$ on $x_{C_3H_8}$. The degree of conversion was varied by varying the temperature for constant τ. The principal characteristic feature of the relations obtained is the linear variation of A, the straight lines on the plot starting from the origin of coordinates. This indicates the constancy of S_{arom} within the limits of each series of catalysts. All the pentasils in the H-form investigated can be divided into two groups. The first contains specimens with Si/Al ranging from 49 to 140; in their presence, propane is converted into aromatic hydrocarbons with the lowest selectivity (S_{arom} = 15%). The second group comprises pentasils with a comparatively high [Al] (Si/Al = 18–24), on which S_{arom} = 28%.

It is noteworthy that the principal pathway followed in the conversion of C_3–C_5 paraffins on decationated pentasils is the cleavage of the molecules of the initial hydrocarbons and reactions involving the resulting C_2–C_3 unsaturated products. For example, on a specimen of the H-TsVK pentasil with Si/Al = 140, the degree of conversion of isobutane at 600 °C reached 60%, whereas $A_{C_4H_{10}}$ did not exceed 13%.[109] The principal isobutane conversion products under these conditions were methane, ethane, and propene, whose overall yield was 40%. Pentane is cracked on pentasils at lower temperatures than propane and isobutane.[112,113] At 450 °C on an H-ZSM-5 specimen with Si/Al = 26, ~50% of pentane is converted into propane with $S_{arom} \simeq 15\%$.[112] As for the transformations of the C_3–C_4 paraffins, the activity of the decationated pentasils in the aromatisation of pentane depends on the composition of the skeleton and increases sharply with increase in [Al]. However, there is a simultaneous increase in the overall degree of conversion, so that S_{arom}, measured for constant x, changes little as Si/Al is varied from 26 to 450.[112]

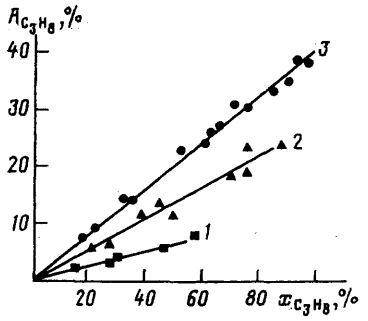


Figure 5. Dependence of the yield of aromatic hydrocarbons on the degree of conversion of propane in the presence of H-pentasils (curves *1* and *2*) and Zn-pentasils (curve *3*) with different Si/Al ratios:[110] *1*, 49–140; *2*, 18–24; *3*, 20–140.

Thus decationated pentasils of different composition are capable of converting C_2–C_5 paraffins into aromatic hydrocarbons, but the ratio of the rates of the target dehydrocyclisation reaction and the cracking side reaction is always appreciably less than unity.

2. Pentasils containing group VIII metals

As mentioned above, catalysts with bifunctional activity, which are active in dehydrogenation and are capable of converting the resulting alkenes into aromatic hydrocarbons, are most suitable for the aromatisation of C_2–C_4 alkanes.

Since decationated pentasils exhibit a high activity in the aromatisation of low-molecular-weight alkenes[3,28,114–124] (and to some extent even paraffins), one might expect that the introduction of a dehydrogenating component into their composition would promote the aromatisation of saturated hydrocarbons. Such bifunctional catalysts should also retain the principal advantages of pentasils—molecular sieve properties[16,17,125] and high resistance to coke formation.

According to patent data,[126] on Pt/H-ZSM-5 at 600 °C ethane is converted to a slight extent into a mixture of benzene, toluene, and xylenes. Detailed study of the catalytic properties of pentasils of the

H-TsVM type, containing Pt, Rh, or Pd, in the aromatisation of ethane and propane[90–97,127–130] led to the discovery of the specific features of the catalytic effect of each element, determined by its nature, in particular the unequal capacities of the M^{n+} cations for undergoing a change in the oxidation state in the oxidation-reduction treatment, and also by the possible differences in the degree of dispersion and in the distribution of the metallic phase within the channels and on the surface of the zeolite component of the catalyst.

It follows from Table 2 that $A_{C_2H_6}$ on Pt/H-TsVM is approximately twice as high as on the initial H-form. On metal-containing pentasils, the reaction proceeds at a lower temperature than on H-TsVM. Comparison with the results obtained on a Pt/Na-TsVM specimen showed that protic acid centres play an important role in the conversion of lower paraffins. If such centres are absent, then the reaction pathway changes radically—the principal ethane conversion products become ethylene and methane, while aromatic hydrocarbons are not formed. It was observed similarly that the main propane conversion product at 300 °C on Pt/Na-ZSM-5 is propene.[131] Catalysts modified by Pd and Rh exhibit a lower activity in the aromatisation of ethane than Pt/H-TsVM.[96,129,130] On raising the temperature to 600 °C, the degree of formation of methane increases and $A_{C_2H_6}$ falls sharply on Rh/H-TsVM.

Table 2. The transformations of C_2H_6 on modified pentasils *.[94]

Catalyst	T, °C	Yield of liquid products, %	Composition of liquid products, %		Composition of gas, %			
			C_5–C_8	C_9–C_{12}	CH_4	C_2H_4	C_2H_6	C_3, C_4
Na-TsVM	600**	0	—	—	2,5	7,5	90	traces
H-TsVM	600	10	95	5	3	1	96	»
0.5% Pt/Na-TsVM	600	traces	—	—	6,5	11,5	82	»
0.5% Pt/H-TsVM	500	10	74	26	18	4	75	3
	600	20	83	17	19	3	78	traces
0.5% Rh/H-TsVM	500	10	85	15	6	2	92	»
	600	2,5	—	—	29	4	67	»
0.5% Pd/H-TsVM	600	2,5	—	—	12	3	85	»
	600**	12,5	54	46	7.5	2,5	90	»

*Flow system, space velocity 120 h^{-1}, treatment of the catalyst with air at 550 °C for 5 h.

**Treatment of the catalyst with air (5 h, 550 °C) and hydrogen (5 h and 550 °C).

Metal–pentasil catalytic systems possess a number of characteristic features. In the first place, the activity of the catalysts depends to a large extent on the conditions in their preliminary treatment. Specimens treated with air or with air and hydrogen in succession are much more active than catalysts reduced directly with hydrogen without preliminary heating in a stream of air (Table 3). The study of the catalyst by X-ray photoelectron spectroscopy (XPES) and electron microscopy made it possible to explain the results of the catalytic experiments.[94,96,97,127–130] Direct treatment with hydrogen leads to the complete reduction of platinum to the zerovalent state and induces the migration of metal particles to the outer surface. Large crystallites, approximately 10 mm in size, are then formed. On heat treatment in air without reduction, approximately 60% of platinum is present as Pt^{2+} ions. Oxidative treatment at 350–500 °C promotes the migration of cations into the interior of the channels. An appreciable proportion of the Pt^{2+} cations then remain in an isolated state. Heat treatment in air is accompanied by the reduction of some of the metal cations to an intermediate or zerovalent state.[130] The Si/Al ratio in the surface layer also increases on heat treatment. This may be caused by the migration of the aluminium outside the skeleton or by the "shielding" of the aluminium as a consequence of the localisation of the cations near the aluminium–oxygen tetrahedra. If the catalysts are treated with air before reduction, it is possible to obtain extremely finely dispersed particles (< 1 nm) with a very narrow distribution with respect to size.[127–130,132] The platinum particle size in the Pt/H-TsVM catalyst was estimated by electron microscopy[127,130,131] and by H_2–O_2 titration,[133] similar results being obtained in both cases. According to the present authors' data,[129] fine metal particles are more active in aromatisation and hydrogenolysis reactions.

Table 3. The influence of the state of the metal and of the degree of its dispersion on the catalytic properties of the M/H-ZSM systems in ethane aromatisation and hydrogenolysis reactions.[129]

M	Treatment of catalyst**	State of metal (%)	Particle size, nm	Aromatisation*		Hydrogenolysis
				yield of AH***, %	S_{arom}	turnover number, s^{-1}
Pt	1	Pt^{2+} (60) Pt^0 (40)	1–2	18	18–20	—
	2	Pt^0 (100)	0,8	15	13–17	9,6
	3	Pt^0 (100)	10	1,5	4,5	0,55
Rh	2	Rh^0 (65) Rh^+ (35)	1–2	13	25	0,54
	3	Rh^0 (75)	3–5	0,9	7.5	0,05

*The aromatisation temperatures for Pt and Rh were 550 and 450 °C; the corresponding temperatures for hydrogenolysis were 420 and 250 °C.

** *1*, At 550 °C in air; *2*, at 550 °C in air and at 450–520 °C in H_2; *3*, at 450–520 °C in H_2.

***AH = aromatic hydrocarbons.

The influence of the conditions in the preliminary treatment of Pt/H-ZSM-5 on the degree of dispersion of the metallic phase has also been observed in other studies.[134–136] According to the data of Engelin et al.,[134] finely dispersed platinum particles (1–2 mm) are formed on slow heating (1 K min^{-1}) of the catalyst in a stream of oxygen diluted with helium. Appreciably larger crystals (⩾10 nm) are formed at a heating rate up to 10 K min^{-1} and only a small proportion of the platinum is localised within the channels. In order to obtain platinum crystallites whose size is less than 1 nm, preliminary stepwise heating of the catalyst in a stream of air (180–300 °C) at a rate of 1 K min^{-1} followed by reduction by

hydrogen and subsequent flushing with nitrogen at 530 °C necessary.[135]

The data examined have shown that the reduction of platinum in pentasils leads, as in faujasites,[137,138] to the localisation of metal atoms or clusters in the zeolite structure and to their partial migration to the outer surface. Such behaviour is also characteristic of the Rh/H-TsVM catalyst.[130]

Another characteristic feature of the catalytic effect of metal-containing pentasils consists in the so-called "running in" of the catalyst during the reaction. This effect is strikingly manifested when aromatisation is carried out under pulse conditions, "running in" not being observed on hydrogen-forms without the metal. One of the possible causes of this phenomenon may be a change in the oxidation state of the metal during the reaction owing to its interaction with the carrier and the catalytic reaction products. The influence of the reaction medium on the formation of the active state of the metal has been investigated in relation to the aromatisation of ethane in the presence of platinum- and rhodium-containing pentasils of the type H-TsVM.[96,97,127,129,130] In order to elucidate the causes of the "running in" phenomenon, a study was made, simultaneously with the study of the catalytic activity of Pt/H-TsVM, of the electronic state of platinum during aromatisation by comparing the X-ray photoelectron spectra of the specimens transferred from the catalytic reactor to the spectrometer. In a specimen heat-treated in a stream of air (Fig. 6, curve *1*), platinum was readily reduced with increase in the number of ethane pulses and the yield of the aromatic hydrocarbons rose and reached a maximum. At this point, the platinum has a positive charge $\delta+$. On a catalyst reduced in a stream of H_2, the nature of the dependence of the yield on the number of pulses remain the same and the maximum yield also corresponded to the appearance of a charge $\delta+$. According to X-ray photoelectron spectroscopic data, the Pt4*f* parameters changed appreciably during the "running in" of the catalyst.[96,127,129,130] Analysis of the photoelectron spectra made it possible to differentiate two types of platinum centres differing in their spectroscopic characteristics: (1) platinum particles whose X-ray photoelectron spectra have been appreciably displaced (by 1.2 eV) relative to the spectrum of the metal; (2) platinum particles in the spectra of which there is no positive shift or a slight negative shift is observed (for example, after ten ethane pulses). It has been suggested[127,129,130] that the positive shift is at least partly due to the transfer of electron density from platinum to the electron-accepting sections of the carrier. During the "running in" of the catalyst, the positive charge on the platinum increases (Fig. 6) and then, after the attainment of the maximum activity, diminishes somewhat, although some of the metallic centres carry a more positive charge both in the initial and in the deactivated specimens.

Large platinum crystallites localised on the outer surface of the zeolite belong to centres of the second type. On the basis of modern ideas concerning the strong interaction of the metal with the carrier,[139] it has been suggested[127,129,130] that under severe reaction conditions (550–600 °C, hydrocarbons, hydrogen), oxygen vacancies may be formed in the pentasil lattice and Al^{3+} ions located in the vicinity of the platinum particles may be reduced. The interaction of platinum atoms or clusters with such electron-donating centres should lead to the appearance of an excess electron density on platinum, which has in fact been observed experimentally by X-ray photoelectron photoscopy.

Summarising data on the state of platinum in Pt/H-TsVM catalysts and taking into account at the same time the change in catalytic properties, one may postulate that there exists a special form of platinum ($Pt^{\delta+}$ with a shift of approximately 1.2 eV) which in fact determines the activity of the catalysts in the aromatisation of ethane.

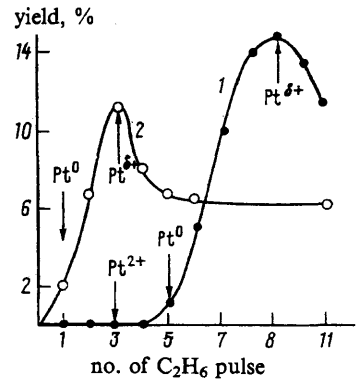


Figure 6. Dependence of the yield of the ethane aromatisation products in the presence of Pt/H-TsVM on the number of pulses:[129] *1*, treatment with air; *2*, treatment with hydrogen.

The Rh-form of the H-TsVM pentasil behaves similarly to the platinum-form.[129,130] After treatment with hydrogen at 400–450 °C, an appreciable portion of rhodium (~40%) in the zeolite remains unreduced. Analysis of the X-ray photoelectron spectra during the aromatisation of ethane demonstrated the presence of two states of rhodium: a state close to the metallic state and one formally corresponding to Rh^+. The change of their relative contributions with increase in the number of ethane pulses is caused by the additional reduction of rhodium and the interaction of the zerovalent metal with the reaction mixture. A similar interaction had been observed earlier for aluminorhodium catalysts of the cyclotrimerisation of ethylene.[130] During the reaction, a significant change in the activity of the catalyst and in the electronic state of the metal occurred. A positive charge arose on rhodium clusters [the maximum shift was $\Delta E_b Rh3d_{5/2} \simeq 0.7$ eV].

A combined study of the catalytic properties of metal-containing pentasils and of the physicochemical properties of the platinum, rhodium, and palladium surfaces[90,92,94–97,127–130] made it possible to elucidate the role of the oxidation state and of the degree of dispersion of metals in the aromatisation of ethane. Evidently the same factors should determine the activity of similar catalysts also in reactions involving C_3-C_4 paraffins. It has been established that the method used to prepare the Pt/H-ZSM-5 catalysts has an appreciable influence on the degree of conversion of propane.[140,141] The specimen obtained by the ion exchange method proved appreciably more active than that in which platinum was introduced by impregnation with a $[Pt(NH_3)_4]Cl_2$ solution. These data were confirmed in other studies.[131,134,135] If part of the platinum is on the outer surface of the zeolite (which is characteristic of catalysts obtained by the impregnation method), then during the first 30–60 min of the experiment these particular metal particles are deactivated and the activity then varies during a long period, since the platinum surface centres located near the structural OH groups are very resistant to coke formation by virtue of the molecular sieve properties of pentasils.[134]

Thus the introduction of noble metals, in the first place platinum, leads to a significant increase in the yield of the products of the aromatisation of lower paraffins and in the selectivity of this process.

3. Pentasils modified by Group II and III elements in the periodic system

As mentioned in the preceding section, pentasils modified by platinum and other noble metals exhibit a high activity in the reactions of lower alkanes, but the selectivity of the aromatisation in their presence does not exceed 30%. In order to increase S_{arom}, pentasils modified by different elements (Ni, Co, Mo, W, Cd, Zn, Ga) were used, but the best results were obtained with the aid of zinc, cadmium, and gallium.[142–152] The modifying elements are introduced in different ways: by ion exchange, by impregnation, by the mechanical mixing of powders, and finally by the isomorphous substitution of aluminium in the lattice with formation of gallosilicates or zinc-silicates.[18,19,80,153–155]

The catalytic properties of Zn/H-ZSM-5 specimens prepared by ion exchange and of the initial decationated form of pentasil have been compared[101,103,156] in propane conversion processes at 450–550 °C and atmospheric pressure. The introduction of Zn^{2+} cations increases $x_{C_3H_8}$ by a factor of 1.5 and S_{arom} by a factor of 2. In aromatic products of the reaction of Zn/H-ZSM-5, the fraction of benzene and toluene is higher, while the content of C_8-C_9 alkylbenzenes is lower than on the unmodified zeolite.[102,103] The proportions of the gaseous hydrocarbons also change appreciably. Modification with zinc leads to a sharp decrease in the degree of conversion of propane into methane and to an increase in the ethane concentration.[101,102,109]

Higher temperature and longer contact times τ are required for the aromatisation of ethane on Zn-pentasils than for the aromatisation of propane. Zinc has an appreciable promoting effect in the aromatisation of ethane on H-TsVM and H-TsVK pentasils with different compositions.[98,157] With decrease in the Si/Al ratio from 32 to 15, $x_{C_2H_6}$ increased at 600 °C and τ = 30 s from 27 to 57%.[157] The maximum value S_{arom} = 35% was obtained on a specimen with Si/Al = 23 at 650 °C. With increase in the aluminium concentration in the zeolite skeleton, the yield of methane and naphthalenes increased and that of hydrogen and C_8 alkylbenzenes fell. On a type H-TsVM (Si/Al = 15) pentasil containing 0.5 wt.% of zinc, $x_{C_2H_6}$ = 32% and $S_{arom} \simeq$ 60% at 600 °C.[98]

Catalysts prepared by the ion exchange method have been used in some studies.[98,101,103] However, the ion exchange capacity of pentasils is low,[158] which precludes the variation of the concentration of the promoting agent within wide limits. According to calculations,[80] the maximum zinc content in pentasil cannot exceed 2 wt.% when the metal is introduced by ion exchange with Na^+ or NH_4^+ ions. Nevertheless the activity of the catalyst should evidently depend on the concentration of the modifying element.[80,117,118,159] A larger amount of the metal can be introduced by the impregnation method into pentasil than by ion exchange. Comparison of the H-TsVK pentasil specimens (Si/Al = 30), containing 0.5, 1.4, and 10 wt.% ZnO showed that the quantities $x_{C_2H_6}$ and $A_{C_2H_6}$ in their presence are greater the higher the zinc content, while in the propane and isobutane conversion reactions the specimens with 1.4 and 10 wt.% ZnO have similar activities.[102]

As in the case of the H-forms, the composition of the skeleton influences the catalytic activity of the Zn-containing pentasils.[103,108–111] On pentasils with Si/Al = 20, 49, 100, and 140, containing 1.5 wt.% Zn, the quantities $A_{C_3H_8}$ and $A_{C_4H_{10}}$ increase appreciably with increase in [Al].[109,110] At the same time, the composition of the skeleton does not affect S_{arom} for catalysts modified with zinc. It follows from Fig. 5 that all the points corresponding to the zinc-containing catalysts with different aluminium contents in the lattice lie on a single straight line starting from the origin of coordinates. The slope of this line corresponds to $S_{arom} \simeq$ 42%, which is greater by 1.5 than on similar unmodified pentasils.

The independence of S_{arom} of x indicates the simultaneous conversion of lower alkanes into aromatisation and cracking products. The increase in S_{arom} as a result of the modification with zinc is caused by the increase in the rate of aromatisation. This relation is evidently independent of the composition of the skeleton of Zn-pentasils and is determined solely by the content of the promoting element in the catalyst.

The composition of the skeleton of Zn-pentasils affects not only the overall catalytic activity but also the ratios of the individual aromatisation products. This is manifested particularly clearly when one examines the isobutane conversion products on pentasils with Si/Al = 20 and 140.[109] The ratios of the concentrations of C_8-C_{10} alkylbenzenes change most significantly. The relative yield of xylenes and ethylbenzenes increases with decrease in [Al]. An important feature of the conversion of lower alkanes on pentasils is the formation of condensed aromatic hydrocarbons, principally naphthalene and its alkyl derivatives. An increase in [Al] in the skeletons of Zn-pentasils favours the formation of naphthalene: the yield of these products at 600 °C is approximately 7 times greater on the specimen with Si/Al = 20 than on the catalyst with Si/Al = 140.

It is known[62,63] that the concentration of the acid centres of pentasils is proportional to [Al] and that their strength is independent of the ratio Si/Al. Consequently the catalytic activity of pentasils of different composition in aromatisation is determined by the number of acid centres, which is consistent with experimental data (see Figs. 4 and 5).

In order to elucidate the role of the acidity of the zeolite carrier in the aromatisation of propane, the catalytic properties of Zn/H-ZSM-5 and Zn/borosilicate specimens were compared.[103] It is known[160–162] that the acidity of borosilicates is significantly lower than that of H-ZSM-5 pentasils. At 550 °C and $P_{C_3H_8}$ = 101 kPa, neither the H-form of the borosilicate nor the borosilicate modified with zinc showed an appreciable activity ($x_{C_3H_8} \simeq$ 1.2–2.0%). The authors explained the inactivity of the H-form by the fact that the weak acid centres of the borosilicate are incapable of activating the propane molecules. However, Zn/borosilicate also proved to be inactive. The aromatisation of propane apparently requires the presence of not only zinc but also of a certain number of acid centres, such as, for example, those in the H-TsVK pentasil with Si/Al = 140.[108–110]

The introduction of another Group II element, namely cadmium, leads to an appreciable rise in activity and S_{arom}. The available information about the promoting effect of cadmium is contained principally in the patent literature.[163–165] A number of studies have been devoted to the systematic investigation of the role of cadmium in the aromatisation of lower paraffins on pentasils.[113,166,167] An almost twofold increase in $A_{C_4H_{10}}$ and S_{arom} has been observed after the introduction of even extremely small (~0.7 wt.%) amounts of cadmium. The degree of conversion of the initial paraffins did not increase after the introduction of cadmium. It is quite likely that the increase in S_{arom} as a result of the modification is associated with the decrease in the cracking activity due to the blocking of the strong protic centres of pentasil by cadmium.

Yet another extremely effective promoting agent for the catalysts of the aromatisation of lower paraffins is gallium.[80,103–105,112,143,144,168–171] According to patent data,[143,144,168] the selectivity of the aromatisation of ethane on Ga/H-ZSM-5 is $S_{arom} \sim 30\%$. An appreciably higher value of S_{arom} (60%) has been observed on the 2% Ga/H-TsVM catalyst at 600 °C and for $\tau \sim 30$ s.[171]

Gallium-containing pentasils, prepared by the ion exchange method, acquire an increased capacity for aromatising lower alkanes after heat treatment in the range 400–700 °C.[80] The influence of the method of preparation of Ga-pentasils on their activity in the aromatisation of C_2-C_4 alkanes has been investigated.[171] Catalysts based on the H-TsVM pentasil (Si/Al = 15) have been prepared in three different ways: by combining the ion exchange of the NH_4^+ cations for Ga^{3+} with subsequent impregnation of the zeolite with the mother liquor (method A); by impregnating the H-form of the zeolite with a solution of gallium nitrate (method B); by the dry mixing of pentasil and gallium oxide powders with subsequent heat treatment in a stream of air at 550 °C by a procedure similar to that of Kucherov and Slinkin[172,173] (method C). Specimen A proved to be the most active, with specimen C showing an appreciably lower activity. A 1:1 mechanical mixture of H-ZSM-5 and Ga_2O_3 has an appreciably higher activity in the aromatisation of propane than pure H-ZSM-5.[174,175]

The catalytic properties of pentasils containing different amounts of gallium in the reactions of C_2-C_5 paraffins have been studied in detail.[103–105,112,170,171,176,177] The introduction of even 0.5 wt.% of gallium appreciably accelerates the aromatisation of ethane and propane and increases A by a factor of 1.3–1.5 compared with the H-form.[171] A gallium concentration of approximately 2 wt.% appears optimal. In the presence of the 2% Ga/H-TsVM catalyst, the quantity A ranges from 30% for ethane to 55–60% for propane and isobutane. In another study,[176] the 6% Ga/H-ZSM-5 catalyst proved to be most active in the conversion of propane. According to Kitagawa et al.,[104] S_{arom} for propane increases sharply after the introduction of ~1 wt.% of gallium and reaches the maximum value (70%) on the 1.6% Ga/H-ZSM-5 (Si/Al = 31) specimen at 500 °C. An even higher selectivity in the aromatisation of propane (up to 85%) on Ga-pentasils was achieved by Tan et al.,[105] S_{arom} being somewhat higher on the Ga/Na-ZSM-5 specimen than on Ga/H-ZSM-5. However, these results do not agree with the data of other investigators[80,103,104,112,170] and are apparently too high.

Ga-pentasils also exhibit a much higher efficiency in the aromatisation of pentane than the decationated specimens.[112] Whereas the maximum value S_{arom} = 38% on H-ZSM-5 (Si/Al = 26) at 600 °C, on the Ga-pentasil with the same composition of the skeleton more than 50% of pentane is converted into aromatisation products. For low degrees of conversion of pentane ($x < 20\%$), the yields of the reaction products on Ga- and H-pentasils are approximately the same. The formation of aromatic hydrocarbons becomes appreciable only for $x_{C_5H_{12}} > 20\%$ and on Ga/H-ZSM-5 the quantities $A_{C_5H_{12}}$ and S_{arom} are significantly higher than on the unmodified catalyst and cracking takes place to an appreciably smaller extent.

The activity of gallium-modified pentasils depends significantly on the composition of the carrier skeleton.[170,177] Active and selective catalysts are obtained only when pentasils with a comparatively high aluminium content (Si/Al = 20) are used. In this case, the values of S_{arom} for isobutane and propane are respectively 60 and 50%. When a carrier with a low aluminium content (Si/Al = 140) is used, S_{arom} diminishes by a factor of approximately 1.5. Similar changes in A and S_{arom} as a function of the Si/Al ratio have been observed also in the aromatisation of pentane.[112] This relation is characteristic only of Ga-pentasils. As mentioned above, on Zn-pentasils with different compositions of the skeleton the aromatisation of propane occurred with identical selectivities.[109,110] The formation of highly active aromatising centres in Ga-pentasils probably requires a combination of a large number of strong B-centres of the carrier and gallium atoms.

The capacity for the activation and aromatisation of lower paraffins is possessed also by certain elementosilicates with the pentasil structure.[18,19,34,153–155,178–187] The modifying element is introduced into such systems in the stage involving hydrothermal synthesis.[37,38] There is then a possibility of obtaining crystalline silicates with a pentasil structure containing skeletal atoms of other elements instead of aluminium. We may note that proof of the isomorphous substitution of silicon atoms in the lattice is frequently either lacking or is inadequate. Gallosilicate, where the presence of Ga atoms in the skeleton has been reliably established by different physical methods, is an exception.[188] These questions have been discussed in detail in a number of communications.[18,19,38] Among the elementosilicates containing Mn, V, Co, Cr, Ti, Ni, Ga, and Zn[179] which have been investigated, the greatest selectivity in relation to aromatisation is shown by zinc-silicates and gallium-silicates.[34,180,181,185–187] On Zn-silicates, where Si/Zn = 140 at 600 °C, V = 2000 h^{-1}, and $N_2/C_3H_8 = 4$, we have $x_{C_3H_8} = 62-64\%$ with $S_{arom} = 43-44\%$.[179,186,187] In contrast to this, the activity and selectivity of Ga-silicates depends to a large extent on the composition of the skeleton. With decrease in Si/Ga from 40 to 15, the quantity $x_{C_3H_8}$ rises from 26 to 84% and S_{arom} increases from 38 to 67%.[34,156,179,186] On the H-ZSM-5 pentasil (Si/Al = 24), S_{arom} did not exceed 30% under similar conditions.[103] Comparison of the results obtained on Ga-silicates and Ga/H-ZSM-5 shows that the isomorphous substitution of silicon by gallium leads to an appreciably greater increase in S_{arom} than treatment with gallium aluminosilicate salts having the pentasil structure.

An important feature of Ga-silicates is the dependence of the activity and selectivity of the conditions on the duration of the reaction and the preliminary activation. With increase in the number of "reaction–regeneration" cycles, both A and S_{arom} in the propane aromatisation reaction on the Ga-silicate increased.[182] According to IR spectroscopic data, such a change in catalytic properties is associated with the emergence of gallium atoms from the skeleton.[182] The increase in the activity of Ga-silicate in the cracking of n-butane after the hydrothermal treatment of the catalyst has been explained by the appearance of extra-skeletal gallium in the form of amorphous Ga_2O_3.[183]

The data presented above referred to Zn- and Ga-silicates synthesised under hydrothermal conditions from reaction mixture in which the aluminium-containing component had been replaced by zinc or gallium salts in the gel-formation stage.[180,181,185,189] Another method of synthesis of gallosilicates has been proposed.[178] It consists in the isomorphous substitution of Si^{4+} ions in the silicalite II lattice (its structure is identical with that of the ZnSM-11 pentasil) by Ga^{3+} cations by treating the silicalite with an aqueous sodium gallate solution at 100 °C. According to X-ray diffraction and NMR spectroscopic data, the material thus obtained is a pentasil containing Ga^{3+} cations in its skeleton. The introduction of gallium into the silicate lattice leads to the manifestation by the latter of an appreciable catalytic activity in the n-butane aromatisation reaction (at 550 °C, $A_{C_4H_{10}}$ = 29%). We may note, however, that the conclusion that silicon ions are substituted by gallium ions[178] was not confirmed in a later investigation.[190]

The use of bimetallic catalysts with the pentasil structure—Pt/Zn-silicates and Pt/Ga-silicates—for the aromatisation of lower paraffins is of great interest.[34,179,180,185] The characteristic features of the catalytic action are determined by the combination of the striking dehydrogenating properties of platinum with the unusual molecular sieve and acid properties of elementosilicates, which are capable of converting C_3-C_5 paraffins and alkenes into aromatic hydrocarbons with a high selectivity. Fig. 7 illustrates the temperature dependence of the degree of conversion of ethane, propane, n-butane, and n-pentane on a Pt/Ga-silicate.[19] Other conditions being equal, the degree of conversion is higher the higher the molecular weight of the paraffin. The quantities S_{arom} are 41.5% for C_2H_6, 57.6% for C_3H_8, 31.9% for n-C_4H_{10}, and 35.8% for n-C_5H_{12}. These results were obtained at 500 °C and $V = 2000\ h^{-1}$ and for a paraffin:carrier gas (nitrogen) concentration ratio of 1:4. In the propane conversion reaction, Pt/Ga-silicates are more active than the initial carriers with Si/Ga = 15–40; the quantities S_{arom} for these systems are similar and are much higher than for the Pt/H-ZSM-5 catalysts.

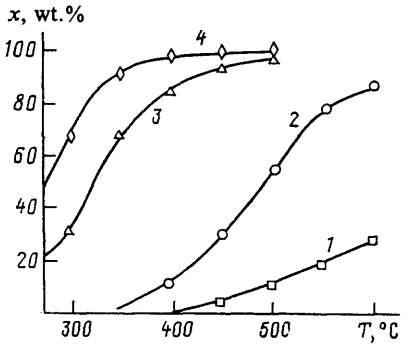


Figure 7. Temperature dependence of the degree of conversion of C_2-C_5 paraffins on the Pt/Ga-silicate catalyst (Si/Ga = 21):[19] *1*, C_2H_6; *2*, C_3H_8; *3*, C_4H_{10}; *4*, C_5H_{12}.

The introduction of platinum into Ga- and Zn-silicates retards the deactivation of the catalysts.[34,178,180] Whereas $x_{C_3H_8}$ fell from 80 to 40% in 10 h on the initial decationated specimens, on platinum-containing catalysts it remained above 50% even after 24 h. Such increase in stability has been attributed[179,180] to the hydrogen spill-over effect.[191–193] The hydrogen activated on platinum can interact with condensed aromatic structures and can "clean" the surface by removing adsorbed condensation products. This hypothesis has been confirmed by the results of a number of studies[133,194,195] in which the role of the hydrogen spill-over in adsorption processes on platinum-, palladium-, and nickel-containing pentasils was investigated. For example, activated hydrogen ("spill-over hydrogen") is capable of displacing chemisorbed CO and CH_4 molecules from the platinum surface.[133,194]

Bifunctional Pt/elementosilicate catalysts are extremely promising for practical use, because they retain their activity in the aromatisation of lower alkanes much longer than other modified pentasils. According to a number of workers,[34,179,196] the activity of the Pt/Ga-silicate catalyst, estimated from $x_{C_3H_8}$, remained unchanged for 1000 h in the "reaction (25 h)–regeneration (0.5 h)" regime at 550 °C and $V = 2000\ h^{-1}$ and for the ratio $C_3H_8:N_2 = 1:4$.

4. The mechanism of the aromatisation of lower paraffins on pentasils

As shown above, the H-forms of pentasils exhibit an appreciable activity in the reactions of C_2-C_5 paraffins. The ability of these catalysts to activate saturated molecules is due to the presence of strong B-centres on which the degradation and conversion of alkenes takes place. Analysis of the dependence of the proportions of the lower paraffin conversion products on the degree of conversion makes it possible to discuss the possible routes to the formation of aromatic and aliphatic hydrocarbons with participation of acid protic centres of pentasils. Fig. 8 presents the dependence of the yields of certain pentane,[112] isobutane,[177] and propane[104] conversion products on x. The character of these curves shows that aromatic hydrocarbons are not the primary reaction products. For low degrees of conversion ($x \leqslant 20\%$), pentane and isobutane are converted into propane with a selectivity in excess of 60%.[113,167]

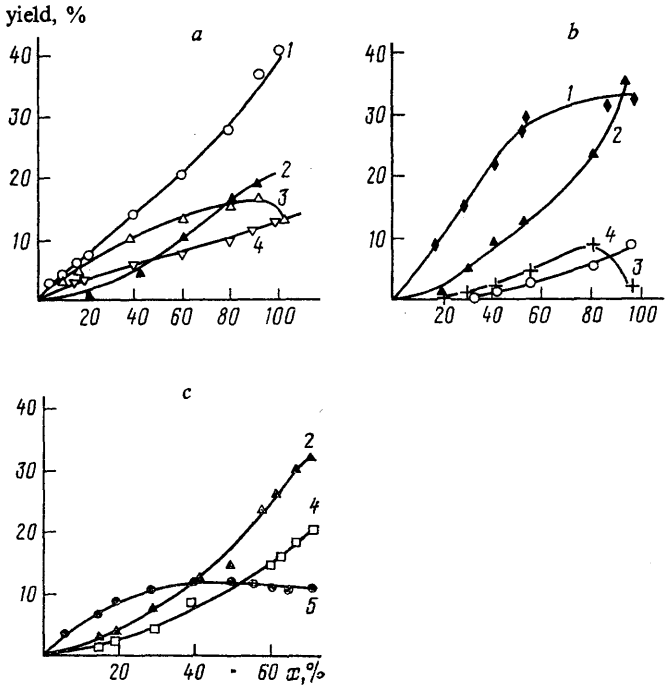


Figure 8. Dependence of the yield of the pentane (*a*), isobutane (*b*), and propane (*c*) conversion products in the presence of H-pentasils on the degree of conversion:[104,112,177] *1*, yield of propane; *2*, overall yield of aromatic hydrocarbons: *3*, overall yield of propene and butenes; *4*, overall yield of ethane and ethylene; *5*, overall yield of ethylene and propene.

Small amounts of propene and butenes are formed simultaneously. The yield of C_3-C_4 alkenes passes through a maximum, which indicates the participation of unsaturated hydrocarbons in subsequent reactions. For $x \leqslant 20-30\%$, propane is converted

mainly into ethylene and methane. These hydrocarbons can be formed via a stage in which propane decomposes to methane and the $C_2H_5^+$ cation with participation of protons in accordance with the scheme

$$C_3H_8 + H^+ \rightarrow \left[\begin{matrix} H_3C \\ \diagdown \\ H \end{matrix} \cdots\cdots CH_2CH_3\right]^+ \rightarrow CH_4 + \overset{+}{C}H_2{-}CH_3.$$

The possibility of the occurrence of this reaction has been demonstrated for the conversion of propane in a strongly acid medium[197] and of C_4 alkanes in the presence of solid superacids.[198]

The question of the contribution of the cracking reaction to the overall conversion of lower alkanes on zeolite active centres is of fundamental importance for the understanding of the mechanism of the catalytic action of decationated pentasils. For low conversions, n-butanes and isobutanes undergo the following transformations:[199]

$$\text{n-}C_4H_{10} \swarrow \searrow \begin{matrix} C_2H_6 + C_2H_4 \\ CH_4 + C_3H_6, \end{matrix} \qquad \text{iso-}C_4H_{10} \rightarrow CH_4 + C_3H_6.$$

Two mechanisms of the cracking of lower alkenes are known: the carbenium ion and radical mechanisms. A scheme taking into account the participation of protic centres in the formation of carbenium ions was presented above. On Lewis acid centres, a hydride ion may be abstracted from the alkane molecule:

$$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2\overset{+}{C}HCH_3 + H^- .$$

According to the results of two investigations,[199,200] the radical reactions of lower alkanes make a considerable contribution on solid amorphous superacids—HU and H-ZSM-5 zeolites. In this case, the initial stage in the cracking process involves the appearance of radical-cations, which are subsequently converted into alkenes. For example, the formation of isobutene from isobutane can proceed via a stage involving the formation and subsequent decomposition of a surface radical-cation with participation of electron-accepting (EA) centres:

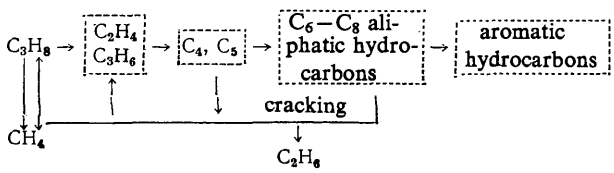
$$\text{iso-}C_4H_{10} + EA \xrightarrow{k_1} [\text{iso-}C_4H_{10}^+][EA^-]$$

$$\begin{matrix} \text{iso-}C_4H_8 + H_2 + EA & C_3H_6 + CH_4 + EA \end{matrix} \quad (k_1 \mid k_2)$$

It is believed[104] that under the conditions of high conversion, propane molecules are activated as a result of the abstraction of a hydride ion by the carbenium ion R^+:

$$C_3H_8 + R^+ \rightarrow RH + \overset{+}{C}H_3CHCH_3.$$

The $C_3H_7^+$ ion formed is converted either into propene or into a carbonium ion with a larger number of carbon atoms. The overall mechanism of the propane conversion reaction on H-ZSM-5 assumes the following form:



Thus the capacity of the decationated forms of pentasils for the deactivation and subsequent dehydrocyclisation of lower paraffin molecules is determined by the presence of strong acid centres on which protonation, hydride ion abstraction, and cracking reactions take place and lead to the formation of unsaturated structures. The reactions of lower paraffins on the acid centres of pentasils apparently proceed with participation of both carbenium ions and radical-cations. The important role of the acidity of the H-forms of pentasils in the aromatisation of lower paraffins is indicated, in particular, by data[104] according to which the dependence of $x_{C_3H_8}$ on the activation temperature in the presence of NH_4-ZSM-5 passes through an extremum. The catalyst heated in a stream of dry air at 580 °C shows the maximum activity. The decrease in the degree of conversion on further increase in the activation temperature is induced directly by the decrease in the concentration of acid hydroxy-groups owing to dehydroxylation.

In contrast to the decationated forms, pentasils modified by Group (II), (III), and (VIII) metals are bifunctional catalysts to the activities of which both the protic acid centres of the carrier and the centres containing metal atoms contribute.

It follows from the data presented that pentasils containing platinum or other Group (VIII) metals are effective catalysts of the aromatisation of lower paraffins and that in terms of activity and selectivity they are superior to the M/Al_2O_3 catalysts. In the first studies on the aromatisation of C_3-C_5 paraffins in the presence of Pt/Al_2O_3, a possible mechanism of this reaction taking into account the bifunctional nature of the deposited metallic catalysts was already proposed.[86,87] We shall examine certain principal conclusions arising from these studies, because the characteristic features of the conversion of lower paraffins on metal-containing pentasils and Al_2O_3-based catalysts are undoubtedly similar.

A consecutive mechanism of the dehydrocyclodimerisation of alkanes includes three stages: (1) the dehydrogenation of alkanes to alkenes and alkadienes; (2) the dimerisation of the alkenes formed—mainly on acid centres and to some extent by a thermal pathway via conjugated dienes; (3) the aromatisation of unsaturated hydrocarbons on the metallic component and on the acid centres. The side reactions are the isomerisation and disproportionation of the aromatic alkyl-substituted products as well as the cracking of the aliphatic hydrocarbons and coke formation. The selectivity in the conversion of lower paraffins into various products must be determined by the relative rates of the individual stages. The set of reactions of n-butane is presented below:[86]

$$C_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_4H_8 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_8H_{16} \xrightarrow{k_3} C_6H_4(CH_3)_2 .$$

$$\downarrow k_4 \qquad \downarrow k_5$$

$$H_4C + C_3C_3 \qquad + C_5$$

According to Csicsery's ideas,[86] on the optimum aromatisation catalyst the rate of dehydrogenation should be higher than the rate of dimerisation ($k_1 > k_2$). In addition, the condition $k_3 > k_2$ should hold and it is most important that the aromatisation should occur much faster than cracking ($k_5 \ll k_3 \geqslant k_2$).

We shall now compare data for the aromatisation of lower paraffins on Pt/Al_2O_3 with the results of kinetic studies[135] on Pt/H-ZSM-5. Analysis of the dependence of the proportions of the isobutane conversion products on the contact time in the presence of 0.8% Pt/Al_2O_3 [76,87] and of the dependence of the yield of propane conversion products on the degree of conversion in the presence of 0.5% Pt/H-ZSM-5 (Fig. 9) shows that in both cases the

aromatisation consists of a set of consecutive and parallel reactions, where the key reaction is the dehydrogenation of the initial paraffin. The presence of an extremum in the variation of the content of the corresponding alkenes (butenes and propene) shows that they are the primary products of the conversion of the alkanes. Both catalysts are extremely active in cracking: the content of C_1-C_2 hydrocarbons exceeds the content of aromatic products, especially on Pt/Al_2O_3. On Pt/H-ZSM-5, S_{arom} can reach very large values, although a considerable proportion of the initial propane is also converted into methane and ethane. The nature of the carrier plays an important role in the aromatisation of saturated hydrocarbons. Whereas alumina is inactive in the reactions of lower paraffins and its activity is low in the aromatisation of alkenes,[201–203] the decationated pentasils readily convert propane and isobutane into aromatic hydrocarbons (see above). Thus both the metallic component and the carrier contribute to the activity of the Pt/H-ZSM-5 catalyst. Another cause of the increased aromatising capacity of Pt/H-ZSM-5 compared with Pt/Al_2O_3 is resistance to coke formation. Whereas Pt/Al_2O_3 is deactivated 15–20 min after the start of the experiment,[76,87] the stable operation of Pt/H-ZSM-5 continues for about 6 h.[134,135]

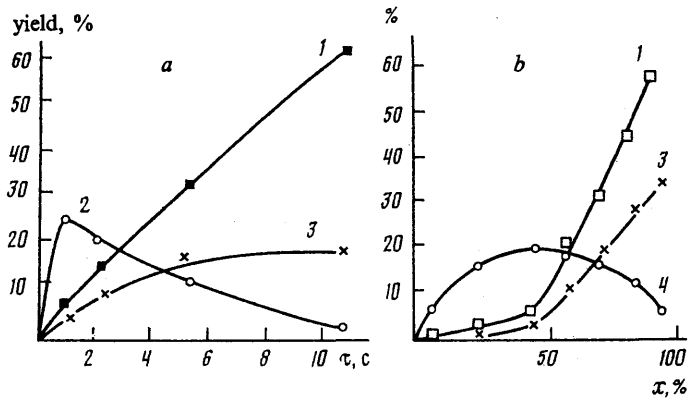


Figure 9. The proportions of the isobutane conversion products on Pt/Al_2O_3 (*a*) at 550 °C and of propane conversion products on Pt/H-ZSM-5 (*b*) at 530 °C:[76,135] *1*, overall yield of methane and C_2 hydrocarbons; *2*, yield of butenes; *3*, overall yield of aromatic hydrocarbons; *4*, yield of propene.

Judging from the data of Gnep et al.,[135] the rate of hydrogenolysis of the initial propane on Pt/H-ZSM-5 is clearly lower than the rate of hydrogenation of ethylene—one of the primary propane conversion products on H-ZSM-5. Thus platinum participates not only in the dissociation of C–C bonds but also in the formation of new C–H bonds as a result of hydrogenation and hydrogenolysis reactions. These two reactions always accompany the aromatisation of lower paraffins on platinum-containing pentasils and are the main cause of the decrease in S_{arom}.

The promoting effect of zinc, cadmium, and gallium as well as the cooperative effect of deposited Group VIII metals are due to the dehydrogenating properties of the M–pentasil systems. Kinetic data, which have been analysed in a number of studies,[104,167,176,177] lead to this conclusion.

Fig. 10 presents curves for the accumulation and consumption of the individual propane, isobutane, and n-pentane conversion products on Zn- and Ga-pentasils. An extremum in the dependence of the yield of C_3-C_5 alkenes on x or τ is characteristic of these catalysts as well as Group VIII metal–pentasil systems, which can be regarded as evidence for the intermediate formation of unsaturated structures from lower paraffins and their subsequent conversion into aromatic hydrocarbons. The principal unsaturated propane conversion product is propene. Apart from butenes, propene is formed from isobutane; olefinic pentane conversion products contain ethylene, propene, butenes, and pentenes.

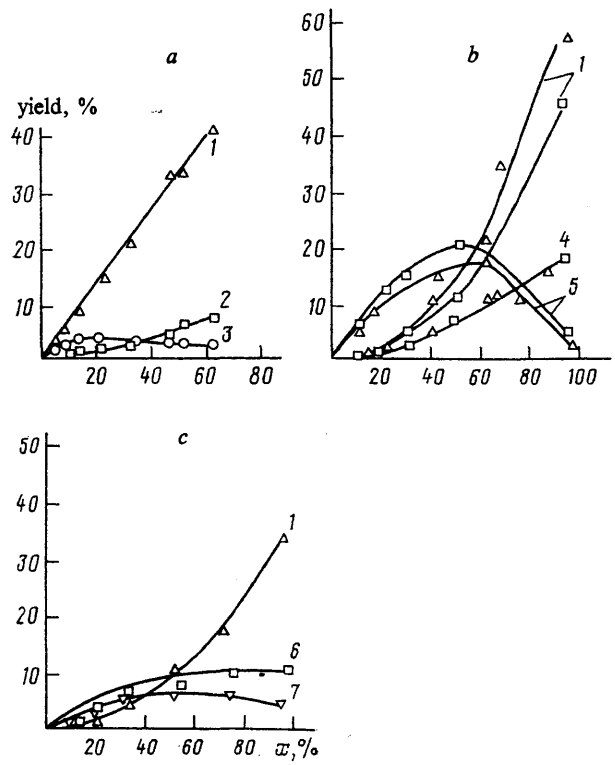


Figure 10. The proportions of the propane conversion products on Ga/ZSM-5 (*a*), the isobutane conversion products on Zn/ZSM-5 (squares) and Ga/ZSM-5 (triangles) (*b*), and the pentane conversion products on Ga/ZSM-5 (*c*) at 500 °C:[112,177] *1*, overall yield of aromatic hydrocarbons; *2*, overall yield of ethane and ethylene; *3*, overall yield of ethylene and propene; *4*, yield of propane; *5*, overall yield of propene and butenes; *6*, overall yield of butanes and butenes; *7*, yield of propene.

According to Bondarenko et al.,[177] under the conditions of low conversion the principal pathway in the reaction of isobutane on Zn- and Ga-pentasils is dehydrogenation, while on the H-form it is cracking. Appreciable amounts of aromatic hydrocarbons are formed only for comparatively high values of $x_{C_4H_{10}}$. Thus $A_{C_4H_{10}} \simeq 10\%$ is obtained for $x \simeq 50\%$ on Ga-pentasil, for 60% on Zn-pentasil, and for 85% on H-pentasil. The results of the calculation of the rate of accumulation of aromatic hydrocarbons for

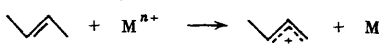
x = const. $\simeq$ 50% showed that the aromatisation of isobutane on Zn- and Ga-pentasils takes place 9 and 12.5 times faster respectively than on the H-form.[177] The activity of Cd-pentasil differs little from the activity of Ga-containing specimens.[166,167]

Thus the aromatisation of lower paraffins on pentasils modified with zinc, cadmium, and gallium includes an alkene formation stage, as happens in the presence of bifunctional platinum-containing catalysts based on pentasil or Al_2O_3. The abstraction of a hydride ion from the alkane molecule with participation of Zn^{2+} cations on the surface (s) may proceed in accordance with the following scheme:[101,108]

$$C_3H_8 + Zn^{2+}_{(s)} \rightarrow \text{iso-}C_3H^+_{7(s)} + [Zn-H]^+_{(s)}.$$

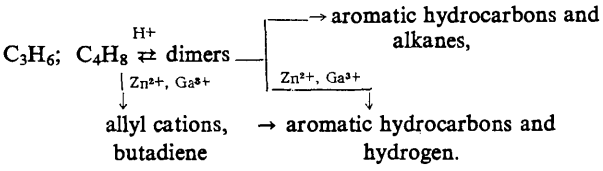
In this case, the zinc cation plays the role of a hydride ion acceptor. According to the result of Kokes and Dent,[204] zinc oxide is capable of effecting the heterolytic dissociation of the C–H bond with formation of intermediate $[Zn-H]^+$ structures. It is generally believed[101,103,105,108–110] that the composition of the paraffin dehydrogenation centres includes promoting elements and that subsequent reactions of the unsaturated compounds formed occur as a result of the interaction of these compounds with protic acid centres of the pentasils. The mechanism of the alkene conversion reactions on pentasils has been discussed in detail in a number of publications.[3,33,119,203,205]

Apart from the first stage (the dehydrogenation of saturated hydrocarbons), zinc and gallium introduced into pentasils participate also in the stage involving the abstraction of a hydride ion from alkene molecules with formation of intermediate allylic compounds.



This conclusion was reached from the analysis of kinetic data for the conversion of but-1-ene into aromatic hydrocarbons on Zn/H-ZSM-5.[206] The introduction of zinc into pentasil led to a sharp increase in S_{arom}. A similar effect has been observed on comparing the activities of H-, Zn-, and Ga-pentasils in the aromatisation of isobutene[170,177] as well as propene.[103] The dependence of the proportions of the but-1-ene conversion products on τ shows that, for low values of x, lower alkenes (ethylene and propene) as well as aliphatic hydrocarbons with a higher molecular weight predominate.[206] These data confirm that the formation of aromatic products is preceded by the oligomerisation of the initial alkene accompanied by the partial cracking of the oligomers. We may note that similar conclusions were reached previously[119,203,207] from the analysis of kinetic data for the conversion of isobutene and propene on type H-TsVK and H-TsVM pentasils. An appreciable amount of butadiene was observed in the but-1-ene conversion products on the Zn-borosilicate catalyst[206] (the selectivity in the formation of butadiene reached 77% for x = 10%), which indicates the dehydrogenation of the initial alkene. The participation of zinc cations in this reaction is confirmed by the finding that the molar ratio of the concentrations of alkanes and aromatic hydrocarbons in the but-1-ene conversion products on Zn-pentasils is 0.9, whereas on H-ZSM-5 it is 2.9. In the presence of Zn-pentasils, the first stage in the activation of but-1-ene may be one involving the formation of allylic (butenyl) structures. The dimerisation of these structures and the subsequent abstraction of hydrogen atoms led to the formation of aromatic hydrocarbons. The capacity of zinc oxides for the formation of allylic structures has been confirmed by spectroscopic methods.[204,208]

On the basis of experimental data, a scheme for the conversion of lower alkenes on pentasils modified with zinc or gallium has been put forward:[206]



Lower alkenes dimerise via the carbenium ion mechanism on the B-centres of decationated pentasils.[3,205,209–211] The dimers can subsequently isomerise and be cleaved to reform the lower alkenes or can be converted into carbenium ions. On subsequent deprotonation and redistribution of hydrogen, aromatic hydrocarbons and alkanes are produced. The formation of one molecule of the aromatic hydrocarbon is accompanied by the formation of three alkane molecules[205] and the yield of alkene aromatisation products is limited by these proportions.

As stated above, in the presence of Zn-pentasils a hydride ion can be abstracted from the molecules of the initial alkenes or converted into allylic intermediates. Aromatic hydrocarbons can be formed in their turn both as a result of the subsequent abstraction of hydride ions from the molecules of alkenes with higher molecular weights (in which the number of carbon atoms is not less than six) and via the direct interaction of two allylic structures with the simultaneous elimination of a hydrogen molecule. This pathway to the formation of aromatic structures does not require the obligatory simultaneous formation of alkanes and therefore in this case the yield of aromatic hydrocarbons is not limited by the stoichiometric relation. This explains the higher yield of the products of the aromatisation of lower alkenes on Zn-pentasils. A similar sequence of transformations of C_2-C_5 alkanes and alkenes is apparently characteristic also of Cd- and Ga-pentasils.

5. The nature of the active centres of the modified pentasils

The results examined in the previous Section show that the modified pentasils possess dehydrogenating properties. In the case of Pt/H-ZSM-5 and other deposited Group VIII metals, the abstraction of hydrogen from saturated molecules takes place with participation of metal clusters dispersed in the zeolite. The nature, structure, and location of the active centres of Zn-, Cd-, and Ga-pentasils are less clear.

As mentioned previously, the catalytic activity of pentasils is determined by the number of acid centres of different nature. Modification with zinc and cadmium alters significantly the acid properties of zeolites. The influence of these promoting agents on the concentration, strength, and nature of the acid centres active in the aromatisation of lower alkanes has been studied in detail.[108–111,166,167,177,212] For this purpose, the hydroxyl coating and the interaction of pyridine molecules with the L- and B-centres of H-, Cd-, and Zn-pentasils, differing in the ratio of the concentrations of aluminium and silicon in the lattice, were investigated by IR spectroscopy.

Three absorption bands with maxima at 3745, 3610, and 3330 cm^{-1} were recorded in the IR spectra of the H-forms of the pentasils in the region of the principal stretching vibrations of the hydroxy-groups.[48–50] They correspond respectively to non-acid silanol and

acid bridging hydroxyls in a free state (3610 cm^{-1}) and in the hydrogen-bonded state (3300 cm^{-1}).[48,50,52] The bands of the acid OH groups in pentasil with Si/Al = 20 are much more intense than in the specimen with Si/Al = 140.[170,177,212]

The introduction of zinc into pentasils leads to some decrease in the intensity of the 3610 and 3330 cm^{-1} bands as a result of the blocking of some of the aluminium–oxygen tetrahedra by zinc cations. Furthermore, an additional absorption band appears at 3520 cm^{-1}. It has been assigned to hydroxyls bound to the Zn^{2+} cations.[212]

Absorption bands referring to the generated pyridinium ions (1550 cm^{-1}, B-centres) and to coordinated pyridine (1448–1453 cm^{-1}, L-centres) have been observed in the range 1300–1600 cm^{-1} in the IR spectra of pyridine adsorbed on H-, Cd-, and Zn-pentasils of the TsVK and TsVM types.[108–111,113,166] By analogy with zeolites of other structural types (faujasites, mordenites, etc.), containing transition metal cations,[39] the band with a maximum at 1453 cm^{-1} in the spectra of all the specimens modified with zinc and cadmium was assigned to pyridine coordinated to the cations of the modifying element. The position of this band is determined by the nature of the cation and the hypsochromic shift (from 1448 to 1453 cm^{-1}) is induced by the increase in the electrostatic field strength and the strength of the aprotic centres.

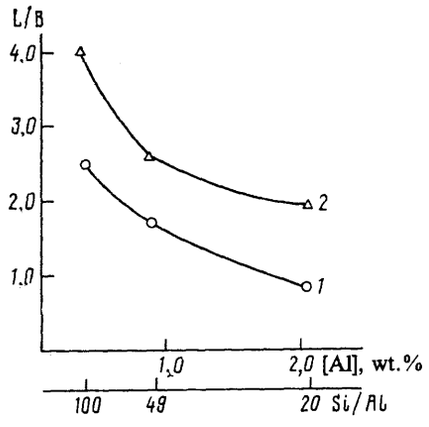


Figure 11. Variation of the L/B ratio with the Al concentration in the skeletons of H-pentasils (curve *1*) and Zn-pentasils (curve *2*).[110]

Fig. 11 illustrates the variation of the ratio of the intensities of these bands (L/B) as a function of [Al] in the lattices of the H- and Zn-forms of the pentasils. A common feature is characteristic of both series of catalysts—the increase in the L/B ratio with increase in Si/Al. This is due to the decrease in the number of B-centres, which is approximately proportional to the number of aluminium atoms in the unit cells of pentasils. As a result of the modification with zinc, the L/B ratio increased by a factor of ~1.5, which indicates the appearance of a large number of new L-centres. A similar picture was observed also for Cd-pentasils. The number of aprotic centres formed depends on the concentration of the promoting agent. Fig. 12 shows how the intensities of the absorption bands of the coordinated pyridine (L), the pyridinium ion (B), as well as the L/B ratio vary with the cadmium concentration. With increase in [Cd] to 2.5 wt.%, L and L/B increase monotonically, while B remains constant. This means that the ratio L/B increases only as a result of the appearance of new L-centres. Further increase in the cadmium content to 5 wt.% lowers the number of protic B-centres, which can be explained by the blocking of the bridging hydroxy-groups by cadmium.

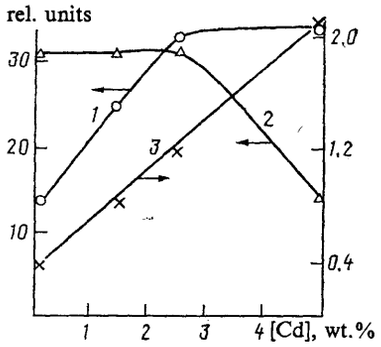


Figure 12. Dependence of L (curve *1*), B (curve *2*), and L/B (curve *3*) on the Cd concentration in type H-TsVM pentasil (Si/Al = 20).[166]

In order to estimate the strengths of the L- and B-centres, a study was made of the thermal desorption of pyridine from the surfaces of pentasils of different composition.[108,111,113] The "(I^t/I°)–desorption temperature" thermal desorption plots are illustrated in Fig. 13.

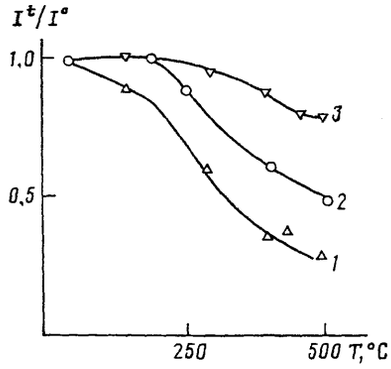


Figure 13. Variation of the relative intensities of the absorption bands of coordinated pyridine as a function of the desorption temperature:[113] *1*, H-TsVM; *2*, 1.5% Cd/H-TsVM; *3*, 1.5% Zn/H-TsVM.

Here I^t is the intensity of the 1448 (1453) cm^{-1} absorption band due to the coordinated pyridine after desorption at the corresponding temperature and I° is the maximum initial intensity of this band before desorption. In the case of unmodified zeolites, an

appreciable desorption of pyridine from the L-centres is observed even at $T < 300$ °C virtually without change in the intensity of the band corresponding to the pyridinium ion; on the other hand, even at 500 °C pyridine remains strongly bound to the B-centres. These data indicate the presence of strong B-centres on the surfaces of the decationated forms of pentasils, which agrees with the result obtained by adsorption microcalorimetry.[61–66] A different picture is observed in the case of pentasils modified with zinc and cadmium. The strength of the coordinate bonds between pyridine and the zinc and cadmium cations is much greater than the strength of the bond with the L-centres of the decationated specimens: more than half the molecules of the adsorbed base remain on the surface at 500 °C.

The properties of the aprotic acid centres of the Zn-pentasils have been investigated by diffuse scattering IR spectroscopy.[170,177,212] Hydrogen (adsorption temperature –196 °C) and carbon monoxide (adsorption temperature 25 °C) were used as probe molecules. The small size of the adsorbate molecules, the large shift of the stretching vibration frequency following polarisation on centres of different nature, the low desorption temperature, and at the same time the possibility of a quantitative determination of the concentration of the active centres impart certain advantages to this research technique.[48,50]

Absorption bands at 4105–4110 and 4125–4130 cm^{-1} have been observed in the IR spectra of hydrogen adsorbed on H- and Zn-pentasils (Fig. 14). They characterise the interaction of molecular hydrogen with bridging and silanol hydroxyls respectively.[46,48–50] Apart from these bands, additional lines appear in the spectra on Zn-pentasils at 3955, 4015, and 4075 cm^{-1}. They refer to complexes of hydrogen with aprotic acid centres of different types. The principal components of such centres are the $Zn^{2+}-O^{2-}$ acid–base pairs.[170,177,212] Since a single line is manifested at 4019 cm^{-1} in the IR spectra following the adsorption of hydrogen on massive zinc oxide,[213] presumably the properties of the ZnO deposited on the surfaces of pentasils differ from those of the massive oxide.

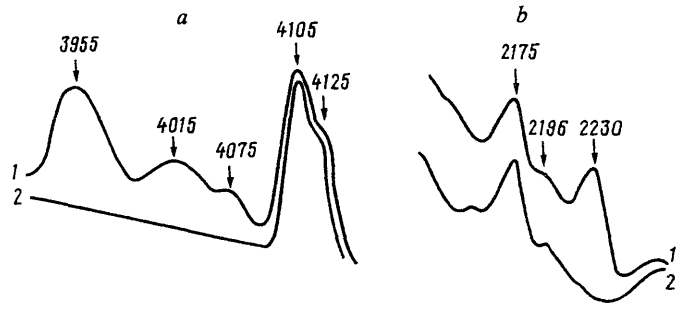


Figure 14. IR spectra of H_2 (*a*) and CO (*b*) adsorbed on Zn-pentasil (curves *1*) and the unmodified H-TsVM (curves *2*).[170,177]

The band at 3955 cm^{-1} undergoes the greatest shift ($\Delta\nu_{H-H}$ = 210 cm^{-1}) relative to the vibration frequency of gaseous hydrogen.[48] It has been shown[212] that at room temperature hydrogen is dissociatively adsorbed on these centres. Furthermore, the $Zn^{2+}-O^{2-}$ acid–base pairs are capable of strongly polarising the C–H bonds in the molecules of lower alkanes. Additional bands at 2805 cm^{-1} (for CH_4) and 2745 cm^{-1} (for C_2H_6), which have undergone bathochromic shifts by 200 and 250 cm^{-1} respectively, have been observed in the IR spectra of methane and ethane adsorbed on Zn-pentasils.[212]

Aprotic acid centres containing zinc cations can be formed on different sections of the pentasil structure. For example, centres to which the absorption bands at 3955 and 4015 cm^{-1} have been attributed are located directly on the aluminium–oxygen tetrahedra, while the band at 4075 cm^{-1} characterises the formation of the ZnO phase which is not linked to the pentasil lattice.

Analysis of the spectra of adsorbed carbon monoxide[177] also leads to the conclusion that new L-centres are formed as a result of the modification of pentasil with zinc (Fig. 14*b*). Bands at 2175, 2195, and 2230 cm^{-1} have been observed in the IR spectra of the modified specimens. The first two bands, present also in the spectra obtained for the H-form, refer respectively to complexes with bridging hydroxy-groups and weak aprotic centres. The band at 2230 cm^{-1} appears only after the introduction of zinc and refers to complexes of CO with fairly strong electron-accepting centres.[42] The preliminary adsorption of molecular hydrogen at room temperature, leading to its dissociation, prevents the appearance of the band at 2230 cm^{-1}, which means that CO is adsorbed on the L-centres responsible for the polarisation of the H–H and C–H bonds in the adsorbed hydrogen molecules and lower paraffins respectively.

Analysis of the IR spectra of adsorbed CO and H_2 demonstrated a fundamental difference in the character of the interaction of these molecules with the acid centres of Zn- and Ga-pentasils.[177,214] Modification with gallium does not lead to the appearance of absorption bands corresponding to aprotic acid centres: the spectra of the H- and Ga-pentasils are identical. The use of other adsorbates (CH_4, CH_3CN) also did not permit the detection of L-centres bound to gallium. It has been suggested[177,214] that one of the causes of the absence of the interaction of these probe molecules with the aprotic centres of Ga-pentasils may be the preferential localisation of gallium on the outer surfaces of the crystallites. It is known[215] that it is very difficult to introduce triply charged cations into pentasils by ion exchange because their solvation shell has a large radius. Furthermore, there is a possibility of electrostatic difficulties associated with the compensation of the isolated negative charges in the lattice by multicharged cations. If gallium is distributed on the outer surface of pentasil, which constitutes approximately 2.5–3.0% of the total surface,[37,38,216] the concentration of centres incorporating Ga^{3+} ions should be low. It is not easy to detect and record such centres by IR spectroscopy owing to the inadequate sensitivity of the method. The paramagnetic probe method,[216–218] based on the analysis of the EPR spectra of various stable radicals adsorbed on the surfaces of catalysts, is much more sensitive. On formation of complexes between radicals and metal ions involved in coordination with low coordination numbers, whose nuclear spin is non-zero, a characteristic EPR spectrum with a hyperfine structure due to the corresponding nuclei is observed. It has been established[177,214,218] that a large (~1.1 nm) stable nitroxyl radical—2,2,6,6-tetramethylpiperidin-1-yloxyl (tanane)—forms donor–acceptor complexes with coordinatively unsaturated Ga^{3+} ions introduced into pentasils. The interaction of the unpaired electron of tanane with the nuclei of the ^{69}Ga and ^{71}Ga isotopes, which have a nuclear spin $I = 3/2$, is characteristic of these complexes. This leads to the appearance of a well resolved quartet with a constant B_{Ga} = 38 Oe for splitting by the gallium nuclei. The results obtained by the paramagnetic probe method show that the coordinatively unsaturated Ga^{3+} cations are localised preferentially on the outer surface of the crystallites,

forming ion pairs of the $Ga^{3+}-O^{2-}$ type. Evidently these cations possess electron-accepting properties like the zinc and cadmium cations located within channels of pentasils.

The aprotic acid centres arising as a result of the introduction of gallium have been detected by the paramagnetic probe method on the outer surface of gallosilicates after they have been heated at 500–600 °C and after the propane aromatisation reaction has been carried out.[182] In this case, the appearance of L-centres is caused by the migration of the extraskeletal gallium onto the outer surface under the influence of the reaction medium.

Electron-accepting centres incorporating gallium ions possess certain specific features which distinguish them from the centres formed by zinc or cadmium cations. Thus, after the successive treatment of a Ga/H-ZSM-5 specimen with hydrogen and oxygen at 450 °C, the ability of the catalyst to adsorb hydrogen increases sharply and the reduction of Ga^{3+} to Ga^{+} is facilitated.[105] According to Guo's data,[169] after Ga-pentasils have been heated in hydrogen at 550 °C, the Ga $2p_{3/2}$ binding energy diminishes by approximately 5 eV, which indicates the partial reduction of gallium. In contrast to this, an appreciable decrease in the Ga $2p_{3/2}$ binding energy was not observed after treatment of the Ga/H-TsVM catalyst with hydrogen, although the composition of the surface layer changed significantly.[171] Under the influence of hydrogen, the surface concentration of gallium diminishes sharply, which may be due to its migration into the bulk phase.

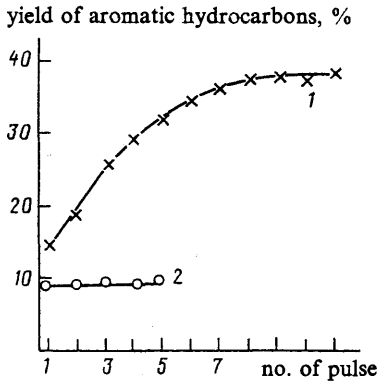


Figure 15. Dependence of the yield of aromatic hydrocarbons on the number of propane pulses:[171] *1*, 2% Ga/H-TsVM; *2*, H-TsVM.

The "running-in" of the Ga-pentasils in the course of the aromatisation of propane under pulse conditions constitutes indirect confirmation of the change in the oxidation state of gallium under the influence of reductants[169,171] (Fig. 15). It is believed[171] that one of the causes of this phenomenon may be the change in the electronic state of gallium resembling the situation arising with platinum and rhodium.[127,129,130] Furthermore, gallium can be redistributed in the zeolite matrix under the influence of the reaction medium. However, we may note that the mechanism of the formation of the active centres in the gallium-containing zeolites requires further study.

Thus one may conclude that, as a result of the introduction of zinc, cadmium or gallium into pentasils, strong L-centres are formed. By virtue of their electron-accepting properties, these are capable of activating the molecules of lower paraffins and of catalysing the dehydrogenation reaction—the key stage in the aromatisation of saturated hydrocarbons.

IV. Application of pentasil-based catalysts in technological processes for the preparation of valuable chemical products from hydrocarbon gases

The dynamics of the development of the manufacture and utilisation of low-molecular-weight hydrocarbons is such that at the beginning of the 1990's an excess of effluent gases from petrochemical industries should arise.[6,7,33] On the other hand, there is an acute problem as regards the rational employment of the components of natural and by-product gases. Such a situation has stimulated the development of new effective processes designed to utilise gaseous hydrocarbons.

Hitherto various foreign companies have suggested several catalytic processes for the conversion of gaseous hydrocarbon raw material in which pentasil-group zeolites are employed. Among them, the following three processes, which are at the introduction stage, may be regarded as the most promising.

(1) MOGD (Mobil Olefin to Gasoline and Distillate) designed to convert gaseous alkenes into high-octane petrol (gasoline) and middle distillates.

(2) "M2-forming" ensuring the formation of concentrates of aromatic hydrocarbons, predominantly the benzene–toluene–xylenes (BTX) fraction from low-boiling alkenes, paraffins, and naphthenes.

(3) "Cyclar"—designed to convert low-molecular-weight paraffins, namely propane and butanes, into aromatic products.

The MOGD process, developed by the Mobil Oil Company is designed to manufacture petrol from diesel fuel.[23,219–221] It is based on reactions involving the oligomerisation of C_2-C_4 alkenes on decationated pentasils of the ZSM-5 and ZSM-11 types.[23,29,30,220,222–224] Information has been published recently concerning the possibility of using borosilicates, ferrosilicates, gallosilicates, silicoaluminophosphates, and other materials with a zeolite structure as catalysts of alkene conversion processes.[19,20,162,225] Under identical process conditions (temperature, pressure, and contact time), the composition of the products formed depends little on the molecular weight of the starting material. Both pure alkenes (ranging from ethylene to hydrocarbons with a boiling point of 204 °C) and various mixtures (fractions) with a fairly high content of unsaturated hydrocarbons can be processed. The liquid catalytic mixture consists of C_5-C_{20} hydrocarbons. The petrol fraction with a high octane number (>85) includes C_5-C_{10} compounds, heavier hydrocarbons being converted after hydrogenation into diesel fuel with a high cetane number (~56).[219] One of the most important features of the MOGD process is the high exothermicity of the alkene oligomerisation reaction—1550 kJ kg^{-1}.[220] In order to remove the heat and maintain isothermal conditions in the reactor, extra-reactor cooling and recirculation of petrol are used. Recirculation results in an increase in the yield of middle distillates. By varying the recirculation conditions, it is possible to regulate the proportions of the petrol and diesel fractions from 100:0 to 10:90.[219,221] Tests of the catalysts on real C_3-C_4 raw

material containing 62% of unsaturated hydrocarbons showed that the reaction products consist of alkenes to the extent of 94%.[219]

Active and stable catalysts based on pentasils of the type H-TsVM and H-TsVK have been developed for the preparation of high-octane petrol from the flame gases in the manufacture of polyethylene (97% ethylene, 2.5% propane).[221,226] During pilot tests, the degree of conversion of ethylene remained at the level of 72–77% for 120 h and the yield of the petrol fraction was 49–57%.

The technological scheme for the MOGD process includes four reactors with a fluidised catalyst bed.[219] The flexibility of the technology, which ensures the possibility of obtaining either petrol or diesel fuel from gaseous alkenes, should be included among the significant advantages of the MOGD process. The process may find extensive applications in petroleum processing, petrochemistry, and the manufacture of synthetic fuels. In the last instance, MOGD can be used in combination with Fischer–Tropsch processes[24,27] or processes for the conversion of methanol into alkenes[26,27] in order to obtain high quality diesel fuel.

The "M2-forming" process is carried out on decationated zeolites of the H-ZSM-5 type at $T > 500$ °C and a pressure of 1–20 atm.[23,227] The ability of the hydrogen-forms of pentasils to convert aliphatic compounds into aromatic hydrocarbons is used in this process. The raw material is a broad fraction comprising C_2–C_8 alkenes and paraffins and containing up to 15% of naphthenes.[227] In contrast to the MOGD process, all the hydrocarbons, except ethane, enter into the aromatisation reactions under the conditions of the M2-forming process. The main bulk of the aromatic products consists of the BTX fraction. The yield of the aromatic pentane and hexane conversion products at 540–580 °C reaches 31–32%. The process includes cracking and hydrogen redistribution reactions, whose contribution increases with increase in temperature.

A common feature of the M2-forming and MOGD processes is a low sensitivity of the composition of the reaction products to the proportions of the components in the starting material.[23] On the other hand, the process temperature is determined by the composition of the starting material. If the initial mixtures are enriched olefins, diolefins, and naphthenes, then aromatic hydrocarbons are formed at comparatively low temperatures. Thus the aromatisation of the petrol fraction of the products of the thermal cracking of low-sulphur masout (12% of aromatic hydrocarbons, 41% of unsaturated hydrocarbons, 47% of paraffin-naphthene hydrocarbons), boiling in the range 35–180 °C, began already at 300 °C.[228] Under these conditions, the content of aromatic hydrocarbons in petrol increased compared with the initial content by a factor of approximately 2. We may note that the content of aromatic hydrocarbons in the M2-forming product can be extremely large, which makes it possible to isolate directly the BTX fraction without an additional extraction stage.[227] For example, petrol having the following composition was obtained at 425 °C:[228] aromatic hydrocarbons—78%, unsaturated hydrocarbons—2%, paraffins and naphthenes—20%. These data indicate a fairly high efficiency of the pentasil-based catalysts in the aromatisation reactions of low-quality petrols obtained as a result of thermodegradative processes.

Apart from low-octane petrols, paraffin-enriched petroleums as well as the effluent gases from petrochemical industries, in particular catalytic cracking gases, can be subjected to the M2-forming process. According to predictions,[227] the M2-forming process together with the MOGD process can become one of the main ways of obtaining high-octane components of motor fuel from olefin-containing gases.

As reported above, modified pentasils are highly effective catalysts of the aromatisation of low-molecular-weight hydrocarbons. Judging from patent data,[142–149] binary catalytic systems are frequently employed for this purpose. Thus, copper, rhenium, platinum, palladium, and gallium are added to stabilise the zinc introduced into pentasils.[144,229–235] A technology for the conversion of light paraffins into aromatic hydrocarbons and hydrogen has been developed by the British Petroleum and the UOP companies in 1984. This process was called "Cyclar".[31–33]

In the "Cyclar" process, active and selective catalysts based on modified pentasils are subjected to constant regeneration, which is ensured by their continuous circulation. As a result, the starting material always comes into contact with the regenerated catalyst and a high level of activity and selectivity is therefore maintained for a long time.

The developments used previously by the UOP Company for the platforming process[31] were used in the technological scheme of the "Cyclar" process. They included a design in which the reactors are placed one on top of the other, a radial flow of the starting material, the use of intermediate heaters, and continuous regeneration of the catalyst. The catalyst for the "Cyclar" process, created on the basis of modified pentasils, satisfies all the principal requirements for industrial catalysts. It is resistant to coke formation and to the action of sulphur, water, and other oxygen-containing compounds and its mechanical strength is high. Either individual propane and butane or propane–propene and butane–butene fractions as well as mixtures of C_2–C_6 hydrocarbons are used as the starting material. On the apparatus for the processing of butane, the yield of aromatic hydrocarbons reaches 67.5% (calculated relative to the starting material which has reacted), while the yield of hydrogen is 5.5%. the overall yield of propane aromatisation products is 63.6%, while the yield of hydrogen is 6%. The proportions of the aromatic propane and butane conversion products are approximately the same. The octane number of the fraction of aromatic hydrocarbons is approximately 112.

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The results examined above indicate considerable advances in the creation on the basis of pentasil-type zeolites of effective catalysts for the aromatisation of lower paraffins as well as progress in the study of the mechanism of their catalytic action and in the development of technological processes for gaining valuable chemical products from hydrocarbon gases. The latest advances in the synthesis of zeolites and zeolite-like materials should constitute a basis for the creation of new more active and more selective catalytic systems.

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α-Fluoroacrylates: synthesis, properties and use

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ABSTRACT. Studies on the synthesis and properties of a new class of monomers—α-fluoroacrylic acid derivatives—are reviewed. Promising areas for the application of synthetic polymeric materials based on α-fluoroacrylates are examined.

The bibliography includes 115 references.

Contents

I. Introduction 906
II. Methods of synthesis of α-fluoroacrylic acid and its derivatives 906
III. Physical and chemical properties of α-fluoroacrylic acid derivatives 911
IV. Properties and use of polymers 914

I. Introduction

Polymers based on acrylates are of fundamental importance in current engineering and technology. In this class of polymers a special position is occupied by poly(methyl methacrylate)—a transparent, impact-resistant, heat-resistant material used in optics. It was known even at the beginning of the 1950's that poly(methyl α-fluoroacrylate) is considerably superior to poly(methyl methacrylate) as regards its physicomechanical properties. However, at that time methods had not been developed for the synthesis of α-fluoroacrylates, which would have provided the opportunity for an extensive study of the properties of materials based on monomers of this class. Research into convenient methods for the synthesis of α-fluoroacrylic acid and its derivatives was systematically conducted in many developed countries of the world during recent decades but it was only in the 1980's that the results of comprehensive studies on poly(α-fluoroacrylates) were published, specifying potential areas of application of these fluoropolymers.

In the present article we review the published studies on α-fluoroacrylates and their polymers with the aim not only of demonstrating the existing progress in this field of chemistry but also of determining the direction of studies that could lead to the very rapid practical application of these excellent synthetic materials.

II. Methods of synthesis of α-fluoroacrylic acid and its derivatives

1. Methods based on condensation reactions of derivatives of fluoroacetic and fluoromalonic acids with carbonyl compounds

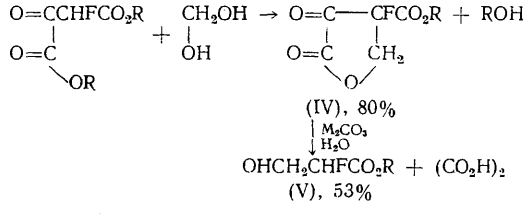
Until recently one of the most widely used methods for the synthesis of α-fluoroacrylates was a method based on a crossed Claisen condensation of alkyl monofluoroacetates with esters of formic and oxalic acid in the presence of strong bases.

The reaction is usually carried out in a solvent (tetrahydrofuran, ether, benzene, methylene chloride) and alkali metal hydrides and alkoxides are used as bases. It is assumed that at the first stage of this reaction nucleophilic addition of a carbanion from fluoroacetate (I) to ester (II) takes place, giving a formyl-, monofluoroacetyl- or oxalyl-acetate (III a–c).[1–5]

$$\underset{\text{(I)}}{CH_2FCO_2R} + \underset{\text{(II)}}{R'CO_2R} \xrightarrow{ROM} \underset{\text{(IIIa–c)}}{R'COCHFCO_2R}$$

R′ = H (a), CH_2F (b), CO_2R (c); R = alkyl (C_{1-7}); M = Li, Na, K.

The majority of the studies in which reproducible results on the synthesis of α-fluoroacrylates have been obtained are based on the use of oxalylfluoroacetates (III c),[6–9] which are condensed with paraformaldehyde to give a lactone (IV). In two studies[6,7] this lactone (IV), R = Et, was isolated and characterised.



Hydrolysis of lactone (IV) in the presence of weak bases (alkali metal carbonates or bicarbonates) gives 2-fluoro-3-hydroxyesters (V).[6–11]

In certain patents the conversion of esters (V) to α-fluoroacrylates (VI) is effected by dehydration.[12,13]

$$\underset{\text{(V)}}{OHCH_2CHFCO_2R} \xrightarrow[-H_2O]{} \underset{\text{(VI)}}{CH_2{=}CFCO_2R}.$$

2-Fluoro-3-hydroxyesters (V) can be converted to esters of 2-fluoro-3-halopropionic acids (VII) by treating them with thionyl chloride or phosphorus tribromide in the presence of pyridine.[14] When treated with bases (hydroxides of alkali and alkaline

earth metals, ammonia, primary, secondary, and tertiary amines), esters (VII) readily eliminate a hydrogen halide to form α-fluoroacrylates (VI).[15,16]

$$\underset{\text{(V)}}{OHCH_2CHFCO_2R} \xrightarrow[C_5H_5N]{SOCl_2(PBr_3)} \underset{\text{(VII)}}{HalCH_2CHFCO_2R} \xrightarrow{\text{base}} \underset{\text{(VI)}}{CH_2{=}CFCO_2R}.$$

Methods for converting esters (V) to the tosyloxy derivatives (VIII) by treating them with *p*-toluenesulphonyl chloride have been reported.[10,11]

$$HOCH_2CHFCO_2R + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow{C_5H_5N} \underset{\text{(VIII)}}{p\text{-}CH_3C_6H_4SO_2OCH_2CHFCO_2R} \xrightarrow[\text{99\%}]{K_2CO_3,\ \text{60\%}} \underset{\text{(VI)}}{CH_2{=}CFCO_2R}.$$

It is also possible to obtain α-fluoroacrylamide by using 2-fluoro-3-tosyloxy derivatives (VIII). In order to achieve this, ester (V) after treatment with ammonia gives 2-fluoro-3-hydroxypropionamide (IX), which is converted to the tosyloxy derivative (X). α-Fluoroacrylamide (XI) is obtained by treating tosylate (X) with sodium methoxide or potassium phthalimide.[10,11]

By dehydrating amide (X) with thionyl chloride in dimethylformamide or trifluoroacetic anhydride it is possible to obtain 2-fluoro-3-tosyloxypropionitrile (XII),[17,18] treatment of which with potassium phthalimide gives α-fluoroacrylonitrile (XIII).

$$\underset{\text{(V)}}{HOCH_2CHFCO_2R} \xrightarrow{NH_3} \underset{\text{(IX), 100\%}}{HOCH_2CHFCO_2NH_2} \xrightarrow[C_5H_5N]{p\text{-}CH_3C_6H_4SO_2Cl} \underset{\text{(X), 92\%}}{p\text{-}CH_3C_6H_4SO_2OCH_2CHFCONH_2} \xrightarrow{\text{base}} \underset{\text{(XI)}}{CH_2{=}CFCONH_2}$$

$$\underset{\text{(XII)}}{p\text{-}CH_3C_6H_4SO_2OCH_2CHFCN} \xrightarrow[\text{DMF}]{SOCl_2,\ \text{60\%}} \xrightarrow[\text{90\%}]{(CF_3CO)_2O} \underset{\text{(XIII), 70\%}}{CH_2{=}CFCN}$$

Nitrile (XIII) can be obtained directly by dehydration of α-fluoroacrylamide (XI) with phosphorus pentoxide, but the yield of nitrile using this method is considerably lower.[9,10]

The synthesis of aryl α-fluoroacrylates based on lactone (IV) is carried out via the isolation of a salt of α-fluoroacrylic acid (XIV).[20,21] This is because in lactone (IV) R can only be an alkyl group and not an aryl group, since alkali metal phenolates are not sufficiently strong bases to be able to initiate the Claisen reaction in the synthesis of lactone (IV). Salt (XIV) is converted to α-fluoroacrylyl chloride (XV) by treatment with benzoyl chloride[11] or with thionyl chloride.[20,21] Reaction of acid chloride (XV) with phenol using trimethylamine as an acceptor of HCl gives phenyl α-fluoroacrylate (VIb). The yield of crude product calculated on the basis of monofluoroacetate (I) is 60% of theoretical.

$$\underset{\text{(IV)}}{O{=}C{<}\begin{matrix}CFCO_2Et\\ CH_2\end{matrix}{>}O{=}C} + NaOH \xrightarrow[-(CO_2H)_2]{} \underset{\text{(XIV)}}{CH_2{=}CFCO_2Na} \xrightarrow[PhCOCl]{SOCl_2,\ 160^\circ C} \underset{\text{(XV)}}{CH_2{=}CFCOCl} \xrightarrow{PhOH,\ Et_3N} \underset{\text{(VIb)}}{CH_2{=}CFCO_2Ph},$$

The nucleophilic addition of dialkyl fluoromalonates to formaldehyde in the presence of bases (piperidine, alkali metal carbonates and bicarbonates) has recently begun to be used for the synthesis of α-fluoroacrylate esters.[19,22–27]

The primary products of this reaction are dialkyl α-fluoro-α-hydroxymethylmalonates (XVI). Esters (XVI) are hydrolysed and decarboxylated in an acidic medium at elevated temperatures. The resulting acid (XVII) is converted to its ammonium salt, and aryl and alkyl α-fluoroacrylates are then obtained by the usual methods (VI).

$$\begin{matrix}CO_2R\\ |\\ CHF\\ |\\ CO_2R\end{matrix} + CH_2O \xrightarrow{KHCO_3,\ H_2O} \underset{\text{(XVI)}}{\begin{matrix}CO_2R\\ |\\ FC{-}CH_2OH\\ |\\ CO_2R\end{matrix}} \xrightarrow[100^\circ C]{HCl} \underset{\text{(XVII)}}{[CH_2{=}CFCO_2H]} \xrightarrow{NH_3} CH_2{=}CFCO_2NH_4.$$

The yield of α-fluoromalonates (VI) does not exceed 50% calculated on the basis of fluoromalonates.

2. Methods based on the reactions of conjugated halofluorination of propene compounds

Since the discovery by Bowers of the method of conjugated halofluorination of unsaturated compounds with *N*-haloamides in anhydrous hydrogen fluoride,[28,29] certain research workers have investigated ways of introducing fluorine into the α-position relative to the carbonyl group.[30–33]

As expected, electrophilic halofluorination of methyl acrylate with *N*-haloamides (*N*-bromoacetamide, 1,3-dibromo-5,5-dimethylhydantoin, hexachloromelamine) in HF gives 3-fluoro-2-halopropionates in moderate yield, regardless of the type of solvent added or reaction temperature (in the range 0 to −78 °C):

$$CH_2{=}CHCO_2Me \xrightarrow[HF]{>N{-}Hal} \underset{\text{30—50\%}}{CH_2FCHHalCO_2Me}$$

2-fluoro-3-halopropionates are only formed in these reactions in small quantities.[33,34] The synthesis of the precursors of α-fluoroacrylates — 2-fluoro-3-halopropionates — is achieved by halofluorination of allyl alcohol, allyl acetate, allyl trichloroacetate.[33,35] The chlorofluorination of allyl alcohol with hexachloromelamine and anhydrous HF in methanol has been studied in the greatest detail.[35,36] Even under optimum conditions for this reaction the yield of 2-fluoro-3-chloropropanol (XVIII) does not exceed 50%. The reaction is accompanied by a large number of side reactions — the formation of isomeric fluorochloropropanol

(XIX), methoxychloro- and dichloro-propanols, and also the oxidation of allyl alcohol to acrolein:

$$CH_2{=}CHCH_2OH \xrightarrow[MeOH,CHCl_3,0°C]{NCl_3,HF} CH_2ClCHFCH_2OH + \underset{(XVIII),\ 45-47\%}{}$$

$$+ CH_2FCHClCH_2OH + CH_3OCH_2CHClCH_2OH +$$
$$(XIX),\ 5-6\% \qquad 9-10\%$$

$$+ CH_2ClCHCH_2OH + CH_2{=}CHCHOCH_3$$
$$\quad OCH_3 \qquad\qquad OH$$
$$5-6\% \qquad 18-25\%$$

Chlorofluoropropanol (XVIII) that is isolated is oxidised in high yield by nitric acid to give 2-fluoro-3-chloropropionic acid (XX), which after dehydrochlorination with a solution of NaOH in methanol and acidification gives α-fluoroacrylic acid (XVII):

$$CH_2ClCHFCH_2OH \xrightarrow[80-100°C]{HNO_3} \underset{(XX),\ 88\%}{CH_2ClCHFCO_2H} \xrightarrow[2)\ H_2SO_4]{1)\ NaOH}$$

$$\longrightarrow \underset{(XVII),\ 60\%}{CH_2{=}CFCO_2H}.$$

Attempts to improve the yield of 2-fluoro-3-chloropropanol (XVIII) by protecting the hydroxyl group of allyl alcohol from being oxidised to acrolein (chlorofluorination of allyl acetate, allyl trichloroacetate and allyl trifluoroacetate) did not produce the desired result,[36] since the yield of the isomeric chlorofluoropropanol (XIX) increased significantly. The presence of this alcohol in 2-fluoro-3-chloropropanol (XVIII) during the subsequent oxidation and dehydrohalogenation gives rise to an impurity that is difficult to separate—α-chloroacrylic acid.[35]

3. Methods based on the fluorination of propene and halopropane derivatives with halogen fluorides

The first attempts to use bromine trifluoride for the synthesis of α-fluoroacrylates were undertaken by Yakubovich et al.[37] Reaction of methyl acrylate with BrF_3 (molar ratio of acrylate to BrF_3 = 2:1) in freon-113 gave a mixture of dihalopropionates with a total yield of 63%:

$$CH_2{=}CHCO_2Me \xrightarrow[freon\text{-}113,0\ °C]{BrF_3} \underset{19\%}{CH_2FCHFCO_2Me} +$$
$$+ \underset{13\%}{CH_2BrCHFCO_2Me} + \underset{31\%}{CH_2FCHBrCO_2Me}.$$

Methyl α-fluoroacrylate was obtained in low yield from this mixture by dehydrohalogenation with triethylamine.

The preparative possibilities of using halogen fluorides for this purpose were investigated again subsequently.[38–42]

The chlorofluorination of methyl methacrylate and allylic esters with a stoichiometric quantity of chlorine monofluoride in inert solvents ($CHCl_3$, CCl_4, CCl_2FCClF_2) has been studied.[38] Under these conditions ClF readily adds to the C=C bonds of these unsaturated esters, although the yield of the α-fluoroacrylate precursors—esters (XXI) and (XXIIIa–c)—does not exceed 50% because of the lack of regiospecificity in addition:

$$CH_2{=}CHCO_2Me \xrightarrow[CHCl_3,\ 25°C]{ClF} \underset{(XXI),\ 28\%}{CH_2ClCHFCO_2Me} + \underset{(XXII),\ 61\%}{CH_2FCHClCO_2Me},$$

$$CH_2{=}CHCH_2OC(O)R \xrightarrow{ClF} CH_2ClCHFCH_2OC(O)R +$$
$$(XXIIIa–c)$$
$$R_a = H\ 30\%$$
$$R_b = CH_3\ 42\%$$
$$R_c = CCl_3\ 50\%$$
$$+ CH_2FCHClCH_2OC(O)R.$$
$$(XXIVa–c)$$
$$18\%$$
$$28\%$$
$$32\%$$

The use of HF as the medium for chlorofluorination in the case of allylic derivatives does not improve the yield of the required regioisomers (XXIIIa–c), while for methyl methacrylate the yield of isomer (XXI) is sharply reduced.[36]

The ability of halogen fluorides to replace a bromine atom on saturated carbon by a fluorine atom is utilised for the synthesis of α-fluoroacrylic acid derivatives.[39–43] In a number of cases this reaction is more selective than addition to a multiple bond. Starting from 1,2-dibromo-3-chloropropane (XXV), which is obtained in quantitative yield by bromination of allyl chloride, methods for the synthesis of two key fluorinated compounds—1-bromo-2-fluoro-3-chloropropane (XXVI) and 1,2-difluoro-3-chloro-propane (XXVIII)—have been developed.[43]

$$CH_2BrCHBrCH_2Cl \text{ (XXV)} \xrightarrow{1/3BrF_3} \underset{(XXVI),\ 60\%}{CH_2BrCHFCH_2Cl} + \underset{(XXVII),\ 25\%}{CH_2FCHBrCH_2Cl}$$
$$\xrightarrow{2/3BrF_3} \underset{(XXVIII),\ 85\%}{CH_2FCHFCH_2Cl}$$

Bromofluorochloropropane (XXVI) is readily separated from its isomer (XXVII). Reaction of (XXVI) with potassium acetate in dimethylformamide in the presence of the phase-transfer catalyst triethylbenzylammonium chloride gives 2-fluoro-3-chloropropyl acetate (XXIX) in good yield. Acetate (XXIX) is readily and in high yield oxidised by nitric acid to 2-fluoro-3-chloropropionic acid (XX), and the latter reacts with thionyl chloride to give the corresponding acid chloride (XXX). In the presence of a catalytic quantity of tertiary amines acid chloride (XXX) gives α-fluoroacrylyl chloride (XV) in high yield.

$$\underset{(XXVI)}{CH_2ClCHFCH_2Br} \xrightarrow[DMF]{AcOK,\ 80°C} \underset{(XXIX),\ 75\%}{CH_2ClCHFCH_2OAc} \xrightarrow[80-100°C]{HNO_3}$$
$$\rightarrow \underset{(XX),\ 85\%}{CH_2ClCHFCO_2H} \xrightarrow[80-100°C]{SOCl_2} \underset{(XXX),\ 90\%}{CH_2ClCHFCOCl} \xrightarrow[100-130°C]{R_3N(5\%)} \underset{(XV),\ 90\%}{CH_2{=}CFCOCl}.$$

High yields of alkyl, fluoroalkyl, aryl, and organophosphorus esters of α-fluoroacrylic acid are obtained by traditional methods from acid chloride (XV).[43–45] α-Fluoroacrylyl fluoride (XXXI) is obtained in a similar manner from difluorochloropropane (XXVIII).

These methods are multistage and the yield of α-fluoroacrylates based on dibromochloropropane does not exceed 35%, but the degree of purity of the monomers obtained in this way is very high.

Methyl α-fluoroacrylate (VIc) can be obtained by a simpler method — from methyl 2,3-dibromo-2-chloropropionate (XXXII).[43]

$$CH_2BrCClBrCO_2Me \xrightarrow[\text{freon-113}]{1/3BrF_3} CH_2BrCClFCO_2Me \rightarrow$$
(XXXII) 85%

$$\xrightarrow[H_2O]{Zn,H^+,100^\circ C} CH_2{=}CFCO_2Me$$
(VI в), 85%

α-Fluoroacrylonitrile (XIII) is readily obtained from 2-fluoro-3-chloropropionyl chloride (XXX):

$$CH_2ClCHFCOCl \xrightarrow{MeOH} CH_2ClCHFCO_2Me \xrightarrow{NH_3} CH_2ClCHFCONH_2 \rightarrow$$
(XXX) (XXI), 95% 90%

$$\rightarrow \xrightarrow[180-250^\circ C]{P_2O_5} CH_2ClCHFCN \xrightarrow{base} CH_2{=}CFCN.$$
70% (XIII), 85%

4. Other methods for the synthesis of α-fluoroacrylates

The most recent method for the synthesis of α-fluoroacrylates is based on the substitution of organobromine derivatives by mercuric fluoride followed by dehalogenation of the fluorine derivative with zinc dust.[46–49] The corresponding esters are formed in very low yield (5–15%).

$$CH_2{=}CHCO_2R \xrightarrow{Br_2} CH_2BrCHBrCO_2R \xrightarrow{quinoline} CH_2{=}CBrCO_2R \rightarrow$$
$$\xrightarrow{Br_2} CH_2BrCBr_2CO_2R \xrightarrow{HgF_2} CH_2BrCBrFCO_2R \xrightarrow[Et_2O]{Zn} CH_2{=}CFCO_2R.$$

Fluoroalkyl α-fluoroacrylates can be obtained in a similar manner from the corresponding acrylate analogues.[50]

The Prince reaction was used in a number of studies for the synthesis of different α-fluoro-substituted propionic acids.[12,13,15,51,52] For example, the condensation of paraformaldehyde with 1,2-difluoro-1,2-dichloroethylene, which takes place most effectively in chlorosulphonic or fluorosulphonic acid, gives the α-fluoroacrylate precursors (XXXIII) and (XXXIV).

$$CClF{=}CClF + CH_2O \begin{cases} \xrightarrow[2)\ HCl,KCl]{1)\ ClOSO_3H} HOCH_2CFClCO_2H \\ \text{(XXXIII), 45—50\%} \\ \xrightarrow[2)\ HCl,KCl]{1)\ FOSO_3H} HalCH_2CClFCO_2H \\ \text{(XXXIV), 45—50\%} \end{cases}$$

The condensation of paraformaldehyde with trifluoroethylene occurs under similar conditions, giving 2-fluoro-3-hydroxypropionic and 2-fluoro-3-halopropionic acids.[13,15] Alkyl α-fluoroacrylates are obtained from these acids by various methods, as described in the previous sections.[12–17]

Subsequent studies on the possibility of using the Prince reaction for the synthesis of α-fluoroacrylates resulted in the development of a new starting compound for this purpose — 2,2,3,3-tetrafluoroxetane (XXXV).[53–57]

$$CF_2{=}CF_2 + CH_2O \xrightarrow[8\ atm]{HF,80^\circ C} \underset{\text{(XXXV), 17\%}}{\overset{CF_2-CF_2}{\underset{CH_2-O}{|\quad|}}} \xrightarrow[DMF]{ROH,NaI,Zn,60^\circ C} CH_2{=}CFCO_2R.$$
(VII), 50—80%

Reaction of tetrafluoroxetane, alkali metal halides, and a dehalogenating agent (molar ratio of 1 : 0.1–1.5 : 0.3–3 respectively) in aprotic bipolar solvents in the presence of a radical polymerisation inhibitor gave α-fluoroacrylyl fluoride (XXXI), which was converted to esters by reaction with the respective alcohols.[55–57] According to the information from patents, the esters can be prepared in one stage without isolation of the acid fluoride. Thus, methyl α-fluoro-deuteroacrylate with a yield of 76% based on oxetane (XXXV) was also obtained by this method.[55]

Original methods for the synthesis of α-fluoroacrylates are based on the addition of chlorofluorocarbene to vinyl ethers.[58–64] Thus, the large-scale synthesis of one of the precursors of α-fluoroacrylates — 2-fluoroacrolein (XXXIX) — has been reported by Molines et al.[58]

$$CH_2{=}CHOR + CHFCl_2 \xrightarrow[Et_4NBr,5^\circ C]{NaOH,CH_2Cl_2,H_2O} \rightarrow$$
$R = n\text{-}C_4H_9$

$$\rightarrow \underset{\text{(XXXVI), 79\%}}{CH_2-\overset{Cl}{\overset{|}{C}}(F)-CHOR} \xrightarrow{C_5H_5N} \underset{\text{(XXXVII)}}{\left[CH_2{=}C(F)-\overset{+}{C}HOR\right]} \xrightarrow{ROH} \rightarrow$$

$$\rightarrow \underset{\text{(XXXVIII), 80\%}}{CH_2{=}CFCH(OR)_2} \xrightarrow{H^+} \underset{\text{(XXXIX), 83\%}}{CH_2{=}CFCHO}$$

Reaction of chlorofluorocarbene with butyl vinyl ether results in the formation of 1-fluoro-1-chloro-2-butoxycyclopropane (XXXVI). Thermal scission of the ring occurs via the formation of allyl cation (XXXVII) to give the dialkyl acetal (XXXVIII), decomposition of which yields fluoroacrolein (XXXIX). This method was used to obtain 15 kg of α-fluoroacrolein.

Fluoroacrolein was subsequently used to prepare phenyl α-fluoroacrylate.[59] The synthesis was conducted in the following manner:

$$CH_2{=}CFCOH \xrightarrow[h\nu]{Br_2} \underset{\text{(XXXIV)}}{CH_2BrCFBrCOBr} \rightarrow$$
(XL)

$$\xrightarrow[C_5H_5N,CCl_4]{PhOH} \underset{\text{(XLI), 78\%}}{CH_2BrCBrFCO_2Ph} \xrightarrow[(iso\text{-}Pr)_2O]{Zn} CH_2{=}CFCO_2Ph.$$
(VIb), 79%

Fluoroacrolein (XXXIX) was mixed with liquid bromine at −5 °C, and the mixture was then refluxed while exposed to UV radiation from a mercury lamp. The resulting acid bromide (XL) was converted in the usual manner to phenyl 2,3-dibromo-2-fluoropropionate (XLI). Dehalogenation of ester (XLI) gives phenyl α-fluoroacrylate (VIb) (61% yield based on α-fluoroacrolein).

A further method for preparing phenyl α-fluoroacrylate (XLII), starting from 1-ethoxy-1-phenoxyethylene, has been developed.[60–64]

$$\underset{\text{(XLII)}}{CH_2{=}C(OEt)(OPh)} \xrightarrow[R_4NCl,CH_2Cl_2]{CHFCl_2,KOH,0^\circ C} \underset{\text{(XLIII), 76\%}}{CH_2-\overset{F}{\overset{|}{C}}(Cl)-C(OEt)(OPh)} \xrightarrow[160\ mm\ Hg]{200^\circ C} CH_2{=}CFCO_2Ph.$$
(VIb), 77%

Table 1. Physical properties of α-fluoroacrylic acid derivatives $CH_2=CFR$.

R	Method of synthesis	Initial compound	Yield, % based on initial compound	b.p. °C (mm Hg)	n_D^{20}	d_4^{20}	Refs.
COOH	II.1	CH_2FCO_2Et[a]	21—26	—	—	—	[11]
	II.2	$CH_2=CHCH_2OH$[b]	13	—	—	—	[35]
	II.4	$CH_2=CHCO_2Me$	5	—	—	—	[46, 49]
C(O)F	II.4	$OCH_2CF_2CF_2$	65—67	—	—	—	[55, 56]
	II.3	$CH_2BrCHBrCH_2Cl$	35—47	28	1.3428	1.2114	[43]
	II.4	$CHF_2CF_2CH_2OH$	45	—	—	—	[65]
C(O)Cl	II.1	CH_2FCO_2Et	10—12	60	—	—	[11]
	II.1	»	45	65—67	—	—	[26, 27]
	II.3	$CH_2=CHCO_2Me$	24	64	1.4070	1.2786	[37]
	II.3	$CH_2BrCHBrCH_2Cl$	25—31	60—64	—	1.2980	[43]
$CONH_2$	II.1	CH_2FCO_2Et[c]	13—24	—	—	—	[10, 11, 19]
	II.1	»[d]	55	—	—	—	[9]
$CON(CH_3)_2$	II.1	»	20	55 (12)	—	—	[11]
CN	II.1	»	17	34—36	—	—	[11, 19]
	II.1	»	10	36	—	—	[9]
C(O)H	II.4	$CH_2=CHOBu$	52.5	71—72	—	—	[58]
	II.4	$CH_2=CHOEt$	38	80—85	—	—	[64]
CO_2Me	II.3	$CH_2=CHCO_2Me$	16	90.5—91.7	1.3880	1.1092	[37]
	II.3	$CH_2BrCBrClCO_2Me$	68	91	1.3915	1.1140	[43]
	II.1	CH_2FCO_2Me	40	95	—	—	[11, 16]
	II.4	$OCH_2CF_2CF_2$ | $CH_2BrCHBrCH_2Cl$	54—56	45 (130)	—	—	[55]
	II.3		26—40	41 (110)	1.390	1.1140	[97]
CO_2CO_3	II.4	$OCH_2CF_2CF_2$ | CH_2FCO_2Et	35—40 (66)	—	—	—	[53]
CO_2Et	II.1		25—41	107—109	1.3940	—	[3, 6, 7, 10, 11]
	II.1	»	64	52 (80)	—	—	[9]
	II.4	$CH_2BrCBrFCO_2Et$	70	110 (728)	1.3940	—	[47, 48]
	II.3	$CH_2BrCHBrCH_2Cl$	26—40	109 (750)	1.3925	1.0555	[43]
$CO_2CH_2CF_3$	II.3	»	—	41 (100)	1.345	1.348	[97]
	II.4	$OCH_2CF_2CF_2$	48	28 (30)	—	—	[55]
$CO_2CH_2CCl_3$	II.4	$OCH_2CF_2CF_2$	46	46 (2)	—	—	[55]
$CO_2CH_2(CF_2)_2H$	II.4	»	49	42 (12)	—	—	[55]
	II.3	$CH_2BrCHBrCH_2Cl$	38	62 (30)	1.360	1.418	[97]
$CO_2CH(CF_3)_2$	II.1	$CHF(CO_2Et)_2$	32	46.8 (160)	1.3145	1.453	[26, 27]
$CO_2CO(CF_3)_2$	II.1	»	34	47 (150)	—	—	[25]
$CO_2CF(CF_3)_2$	II.1	»	32	40 (123)	—	—	[25, 26]
$CO_2CH_2CF(CF_3)_2$	II.3	$CH_2BrCHBrCH_2Cl$	26—40	122 (760)	1.331	1.507	[97]
$CO_2C(CH_3)_2CF_2CF_2H$	II.3	»	—	63 (30)	1.377	1.514	[97]
$CO_2CH_2(CF_2)_4H$	II.4	$OCH_2CF_2CF_2$ | $CH_2BrCHBrCH_2Cl$	47	38—42 (4)	—	—	[55]
	II.3		26—40	70 (21)	1.347	1.548	[43, 97]
$CO_2CH_2(CF_2)_6H$	II.3	»		97—101 (17)	1.342	1.632	[97]
$CO_2(CH_2)_2(CF_2)_8H$	II.4	$OCH_2CF_2CF_2$ | »	47	86 (4)	—	—	[55]
$CO_2CH_2(CH_2)_4CH_2$ | CO_2Ph	II.4	»	37	53 (4)	—	—	[55]
$CO_2CH_2C(Me)_2CH_2CH(Me)CH_2$	II.4	»	52	48 (2)	—	—	[55]
	II.4	»	42	43—46 (2)	—	—	[55]
	II.4	$CH_2=CHOEt$	40	52—54 (0.5)	—	—	[60, 63, 64]
	II.4	$CH_2=CFC(O)H$	61.5	52—54 (0.5)	—	—	[58]
	II.1	CH_2FCO_2Et	60[g]	40 (0.2)	—	—	[20, 21]
	II.3	$CH_2BrCHBrCH_2Cl$	26—40	78 (5)	1.5030	1.1756	[43]
$CO_2C_6F_5$	II.3	»	—	59 (3)	1.426	1.549	[97]
	II.1	$CHF(CO_2Me)_2$	38	41—42 (1.5)	—	—	[24]
$CO_2C_6Cl_5$	II.1	»	42	—	—	—	[24h]
$CO_2C(CF_3)_2C_6H_5$	II.1	»	26	66 (4)	—	—	[25h]
CO_2–*p*-$C_6H_4P(O)(Ph)_2$	II.3	$CH_2=CFCOCl$[f]	—	—	—	—	[44, 45i]
$CO_2CH_2CH_2OH$	II.2	$CH_2=CHCH_2OH$	21	81—83 (3)	1.4365	1.2318	[9j]
$CO_2CH_2CH(OH)CH_3$	II.2	»	21	66—68 (3)	1.4328	1.1688	[9j]
$CO_2CH_2CH(OH)CH_2Cl$	II.2	»	21	90—93 (4)	1.4631	1.3200	[9j]

Note. [a] m.p. = 50—51 °C; [b] m.p. = 51.5—52 °C; [c] m.p. = 115—116 °C; [d] m.p. = 116 °C; [e] m.p. = 93—95 °C; [f] m.p. = 114—144.5 °C; [g] yield of crude product is given. [h] Heumüller et al.[24] also report the m.ps. and b.p. of other esters with the formula $CH_2=CFCO_2R$, where R = *o*-, *m*-, and *p*-substituted phenyl groups. [i] In one patent[25] b.ps. are given for compounds with the general formula $CH_2=CFCO_2C(CF_3)_2R$, where R = *m*- and *p*-substituted phenyl groups, furyl and thienyl groups. [j] Lapin et al.[44,45] also give the m.ps. of α-fluoroacrylates of the *ortho*- and *meta*-derivatives of hydroxyphenyldiphenylphosphine oxide.

The unsaturated acetal (XLII), on reaction with chlorofluorocarbene, forms 1-fluoro-2-phenoxy-1-chloro-2-ethoxycyclopropane (XLIII). Thermolysis of cyclopropane (XLIII) under vacuum gives phenyl α-fluoroacrylate (VIb) in good yield.

Recently an original three-stage method for the synthesis of α-fluoroacrylyl fluoride (XXXI) from tetrafluoro- and trifluoro-chloro-propanol was proposed.[65]

$$\underset{\text{(XLIV)}}{HCFXCF_2CH_2OH} \xrightarrow{2RLi} \underset{\text{(XLV)}}{CFX{=}CFCH_2OH} \xrightarrow{H^+} \underset{\text{(XXXI)}}{CH_2{=}CFCOF}.$$

X=Cl, F; R=Me, Bu.

At the first stage alcohol (XLIV) is dehydrofluorinated by alkyl lithium and the resulting allyl alcohol (XLV) is converted to acid fluoride (XXXI) by heating with concentrated sulphuric acid.

III. Physical and chemical properties of α-fluoroacrylic acid derivatives

1. Physical properties

During the last few years a large number of α-fluoroacrylic acid derivatives—halides, amides, nitriles, and alkyl, fluoroalkyl, and aryl esters—have been obtained. The syntheses of most of these compounds have been carried out mainly in order to obtain from them homo- and co-polymers with valuable properties. Therefore, most of the available data on the properties of α-fluoroacrylic acid derivatives appears in patent literature and only a few scientific publications have been devoted to a study of the chemical properties of alkyl and fluoroalkyl α-fluoroacrylates. All of the published data on the physical properties of α-fluoroacrylic acid derivatives are given in Table 1, with the methods of preparation, yields of these monomers, and the literature sources being indicated.

2. Heterolytic reactions of α-fluoroacrylates

Information about the reactivity of α-fluoroacrylate esters towards nucleophilic and electrophilic reagents is extremely limited.[41,47,66,67] Nucleophilic reagents such as alcohols, mercaptans, malonate and acetaminomalonate esters in the presence of alkali metal alkoxides readily add to ethyl α-fluoroacrylate. The direction of addition is such that the nucleophile adds to terminal electron-deficient methylene group of the C=C double bond:[66]

$$CH_2{=}CFCO_2Et \left\{ \begin{array}{ll} \xrightarrow{EtOH,EtONa} & EtOCH_2CHFCO_2Et \ (66\%) \\ \xrightarrow{BuSH,BuOK} & BuSCH_2CHFCO_2Et \ (90\%) \\ \xrightarrow{CH_2(CO_2Et)_2,EtONa} & (EtOCO)_2CHCH_2CHFCO_2Et \ (41\%) \end{array} \right.$$

This is completely analogous to the direction of addition of nucleophiles to unsubstituted acrylates and α-chloro- and α-bromo-acrylates.[68]

Ammonia and amines do not add to the C=C bond of ethyl α-fluoroacrylate but give α-fluoroacrylamides,[66] whereas ammonia readily adds to alkyl α-bromoacrylates to form 2-bromo-3-amino-propionate esters.[69]

Electrophilic reagents such as nitronium fluoride,[66] mercuric nitrate,[66] and bromine monofluoride[41] can also add to the carbon–carbon double bonds of alkyl α-fluoroacrylates. In contrast to unsubstituted acrylates,[70] α-fluoroacrylates add the positively polarised residues of electrophilic reagents to the β-carbon atom:

$$CH_2{=}CFCO_2R \left\{ \begin{array}{ll} \xrightarrow{HNO_3,HF} & O_2NCH_2CF_2CO_2R \ (53\%) \\ \xrightarrow[EtOH]{Hg(NO_3)_2} & O_2NOHgCH_2CFCO_2R \ (48\%) \\ & \quad | \\ & \quad OEt \\ \xrightarrow{1/3(BrF_3+Br_2)} & CH_2BrCF_2CO_2R \ (39\%) \end{array} \right.$$

Electrophilic reagents add to methyl α-chloroacrylate in a similar manner.[41,66] However, the direction of addition of such typical electrophiles as methyl- and phenyl-sulphenyl chlorides to alkyl α-fluoroacrylates is different—the alkylthio and arylthio residues mainly add to the α-carbon atom.[67]

$$CH_2{=}CFCO_2Et \left\{ \begin{array}{ll} \xrightarrow{MeSCl} & CH_2ClCF(SMe)CO_2Et \ (90\%) \\ \xrightarrow{PhSCl} & CH_2ClCF(SPh)CO_2Et \ (68\%) + PhSCH_2CFClCO_2Et \ (22\%) \end{array} \right.$$

Methyl α-fluoroacrylate does not absorb molecular chloride but in the presence of 1–2% tetramethylammonium bromide the reaction with chlorine is very vigorous with evolution of heat, and subsequently on heating α-fluoroacrylate almost the theoretical quantity of Cl_2 is absorbed. It appears that this reaction does not occur by an anionic mechanism as was previously thought[71] but by a free-radical mechanism, since the dimers formed as by-products on chlorination have a structure identical to radical telomers of acrylates:[72]

$$CH_2{=}CFCO_2Me \xrightarrow[Me_4NBr]{Cl_2} CH_2ClCFCO_2Me \xrightarrow{Cl_2} CH_2ClCFClCO_2Me$$

$$CH_2ClCFCO_2Me \xrightarrow{CH_2{=}CFCO_2Me} \underset{\displaystyle\xrightarrow{Cl_2}}{CH_2ClCFCO_2Me} \quad CH_2ClCFCO_2Me$$

$$\begin{array}{ll} CH_2CFCO_2Me & CH_2CFClCO_2Me \end{array}$$

Methyl α-chloroacrylate is chlorinated in a similar manner, whereas methyl methacrylate reacts with Cl_2 by an electrophilic mechanism and forms chlorinated dimers through the formation of new C–O rather than C–C bonds.[71]

3. Free-radical reactions of α-fluoroacrylates

a) Radical polymerisation

As was noted in the previous section, the syntheses of α-fluoroacrylic acid derivatives are complex and have multiple stages, so the preparation of significant quantities of the highly pure monomers necessary for studying the kinetics of polymerisation is an extremely laborious process. It is likely that as a result of this, systematic studies on the kinetics of polymerisation of α-fluoroacrylic monomers have not been carried out. Up to the present time only a few studies devoted to this subject have been carried out.[73–79]

Thus, Yamada et al.[73] have studied the radical polymerisation of ethyl α-fluoroacrylate (EFA) in bulk at 30 °C. The fundamental rate constants for chain propagation (K_p) and chain termination (K_t) have been determined, and these are given in Table 2. For comparison, the rate constants for chain propagation and chain termination of other α-substituted acrylates are also shown in Table 2.

The radical copolymerisation of ethyl α-fluoroacrylate with a number of vinyl monomers has been studied and the copolymerisation rate constants determined. From these data it was possible to calculate the fundamental rate constants $K_{2,1}$ and $K_{1,2}$ for ethyl α-fluoroacrylate and the poly(ethyl α-fluoroacrylic) radical. These results and also the corresponding rate constants for methyl acrylate (MA) and ethyl α-chloroacrylate (ECA) are given in Tables 3 and 4.

Table 2. Rate constants of chain propagation (K_p) and termination (K_t) for α-substituted acrylates at 30 °C.[73]

$CH_2=C(X)CO_2R$		$K_p^2/K_t\times10^3$, litre mol^{-1} s^{-1}	K_p, litre mol^{-1} s^{-1}	$K_t\times10^7$, litre mol^{-1} s^{-1}
X	R			
Cl	Et	8.27	1660	48.0
F	Et	2.58	1120	33.3
Me	Me	4.82	450	4.2
H	Me	0.16	720	0.43

Table 3. Reactivity of polymer radicals towards MA, EFA, and ECA at 30 °C.[73]

Monomer	$K_{2,1}$, litre mol^{-1} s^{-1}				
	polystyrene	poly(MMA)	poly(MA)	poly(EFA)	poly(ECA)
MA	141	176	720	6588	516
EFA	240	216	1000	1120	272
ECA	1514	940	7579	5333	1660

Table 4. Reactivity of monomers towards polymer radicals of MA, EFA, and ECA at 30 °C.[73]

Radical	$K_{1,2}$, litre mol^{-1} s^{-1}					
	styrene	MMA	MA	EFA	ECA	AN
poly(MA)	4000	2182	720	1000	7200	1004
poly(EFA)	6222	3394	6588	1120	5333	1120
poly(ECA)	5533	830	520	516	1660	572

[AN = acrylonitrile].

An analysis of these data shows that ethyl α-fluoroacrylate is 3–7 times less reactive than ethyl α-chloroacrylate and has a similar reactivity to that of methyl acrylate. Comparison of the reactivity of the polyradicals of MA, EFA, and ECA also reveals the similarity between the poly(methyl acrylic) and poly(ethyl α-fluoroacrylic) radicals, which are more reactive than the poly(ethyl α-chloroacrylic) radical. These characteristics apparently occur because the fluorine atom stabilises the resulting radical to a much lesser degree than the chlorine atom. This results in ECA having a higher reactivity than EFA and correspondingly the polymer radical of ECA being less reactive than the poly(ethyl α-fluoroacrylic) radical. Gal'perina et al.[76] studied the effect of the solvent on the rate constants of chain propagation and termination in the radical polymerisation of acrylic acid (AA) and α-fluoroacrylic acid (FAA). Water, formamide, and DMSO were used as solvents. The results are given in Table 5.

Table 5. Rate constants of propagation and termination for the polymerisation of AA and FAA in different solvents at 20 °C.[76]

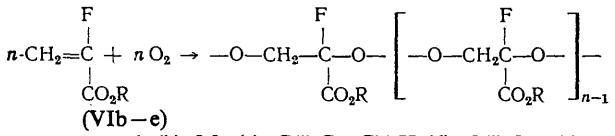
Solvent	FAA		AA	
	K_p, litre mol^{-1} s^{-1}	$K_t\times10^{-8}$, litre mol^{-1} s^{-1}	K_p, litre mol^{-1} s^{-1}	$K_t\times10^{-8}$, litre mol^{-1} s^{-1}
Water	2600±200	0.87±0.07	27 200±200	1.8±0.15
Formamide	2200±200	0.74±0.07	4 200±20	1.0±0.2
DMSO	850±50	0.49±0.01	500±50	0.2±0.01

As can be seen from the results presented, the rate constants of propagation decrease on going from water to DMSO, which is due to the fact that DMSO has the greatest capacity to form complexes with a polymer radical. The marked difference between the values of K_p in the polymerisation of FAA and AA in water is apparently governed by the reactivity of the polymer radicals. The presence of a fluorine atom at the α-position causes a reduction in density of the unpaired electron in a polymer radical, which results in a decrease in reactivity of the polymer radicals of FAA. The difference between the values of K_p in polymerisation between a polymer radical and solvent is considerably less. In the polymerisation of FAA the probability of forming such a complex is much less than in the polymerisation of AA, which leads to a greater decrease in reactivity of AA.

The kinetics of the polymerisation of 2,2,3,3-tetrafluoropropyl α-fluoroacrylate (FN-1) and its methacrylate analogue were recently studied.[79] It was shown that under the same conditions 2,2,3,3-tetrafluoropropyl α-fluoroacrylate polymerises at a much higher rate than 2,2,3,3-tetrapropyl methacrylate (MN-1) and its polymerisation is accompanied by a greater reaction enthalpy. Thus, K_p/K_t is 1.15 (litre mol^{-1} s^{-1})$^{0.5}$ for FN-1 and 0.22 (litre mol^{-1} s^{-1})$^{0.5}$ for MN-1. The polymerisation enthalpy is equal to −73 kJ mol^{-1} for FN-1 and is −57 kJ mol^{-1} for MN-1.

b) Autooxidation by atmospheric oxygen

α-Fluoroacrylates, in the same way as other vinyl monomers,[80–82] are oxidised by atmospheric oxygen to give peroxides that consist of alternating copolymers of monomers and oxygen.[83,84]



(VIb–e)

R = Ph (b), Me (c), $CH_2CF_2CF_2H$ (d), CH_2CF_3 (e); $n = 10 - 20$.

Other conditions being equal, α-fluoroacrylate esters absorb oxygen much more rapidly (by a factor of 100 or more) than their acrylate and methacrylate analogues (Table 6). It would appear that there are no parallels amongst acrylic or other vinyl monomers with respect to the rate of oxidation of α-fluoroacrylates by air.

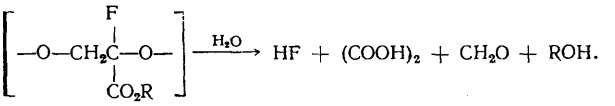
Table 6. Absolute and relative rates of oxidation (W) of monomers $CH_2=CXCO_2R$ by atmospheric oxygen at 50 °C (concentration of initiator AIBN = 8.6×10^{-2} mol litre^{-1}).[83]

Monomer		$W \times 10^5$, mol litre^{-1} s^{-1}	W_{rel}
X	R		
H	$CH_2(CF_2)_2H$	0.05	1
Me	$CH_2(CF_2)_2H$	0.17	3.4
F	Me	10.7	210
F	$CH_2(CF_2)_2H$	11.9	240
F	CH_2CF_3	43.0	360

In two studies[4,5] the greatest attention was given to phenyl and tetrafluoropropyl esters of α-fluoroacrylic acid and to the properties of their polyperoxides. The rate of oxidation of tetrafluoropropyl α-fluoroacrylate initiated by azobis(isobutyronitrile) (AIBN) on temperature was studied and the ratio of the rate constants of chain propagation (K_p) and chain termination (K_t) was calculated as $(K_p/K_t) = 7.4 \times 10^3 e^{-7034/RT}$.

As is evident from this equation, the oxidation of tetrafluoropropyl α-fluoroacrylate over the temperature range 40–60 °C has an energy of activation (7 kcal mol^{-1}) that is much lower than that of methyl methacrylate (10.5 kcal mol^{-1}).[80]

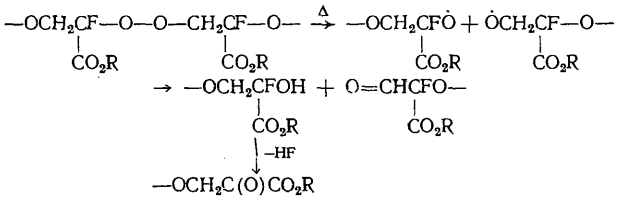
The peroxides of fluoroalkyl and aryl α-fluoroacrylates readily decompose when treated with nucleophilic reagents such as alkalis, alcohols, and water. The hydrolysis products of the peroxides of tetrafluoropropyl and phenyl α-fluoroacrylate provide confirmation that their structure consists of alternating copolymers with oxygen:



R = Ph (VIb), $CH_2CF_2CF_2H$ (VId)

The hydrolytic decomposition of the peroxides of these monomers in dioxan and tetrahydrofuran occurs at temperatures considerably below the temperature range of their thermal decomposition.[83,84]

The thermolysis of peroxides of tetrafluoropropyl and phenyl α-fluoroacrylates takes place with the evolution of gaseous HF (0.5 to 0.8 moles per mole equivalent of peroxide). Panteleeva et al.[83,84] attribute the evolution of HF to the disproportionation of primary radicals in the solvent cage, as a result of which unstable fluorohydroxy compounds are formed:



The kinetics of the thermal decomposition of peroxides of phenyl and fluoroalkyl α-fluoroacrylates in hydrophobic solvents have been studied. Kinetic data on the thermolysis of these peroxides correlated against similar data on their acrylate, methacrylate, and α-chloroacrylate analogues and benzoyl peroxide are given in Table 7.[83–85] It is clear from these data that the temperature range of thermolysis of peroxides of α-haloacrylates is considerably lower than for their acrylate and methacrylate analogues. The thermolysis characteristics of α-fluoroacrylate peroxides are similar to those of the widely used medium-temperature radical initiator—benzoyl peroxide. It is probable that the high rate of oxidation of α-fluoroacrylates at normal temperatures is due to the relatively low temperature range of thermal decomposition of their own peroxides, as a result of which these peroxides effectively initiate the radical chain autooxidation of the monomers.

Table 7. Kinetic data on the thermal decomposition of peroxides $-(-OCH_2CXO-)-$ in solution* (initial concentration of peroxides = $4-20 \times 10^{-2}$ equivalents litre^{-1}.

No.	X	R	T, °C	$K \times 10^5$, s^{-1}	E, kcal mol^{-1}	Refs.
1	H	Ph	120.0	8.3	28.0	[85]
2	Me	Ph	100.0	6.8	32.4	[85]
3	Cl	Ph	75.3	7.9	25.6	[85]
4	F	Ph	75.0	2.9	27.5	[84]
5	F	$CH_2(CF_2)_2H$	73.0	5.6	31.5	[83]
6	F	CH_2CF_3	72.5	8.2	29.9	[83]
7	benzoyl peroxide		79.9	3.3	32.7	[86]

*Peroxides 1–4 and 7 in chlorobenzene, peroxides 5 and 6 in $MeCO_2CH_2CF_2CF_2H$.

Thus, the low thermal and hydrolytic stability of α-fluoroacrylate polyperoxides assists on the one hand the rapid formation of polyperoxides in monomers and on the other hand their rapid

decomposition, which accompanies the formation of decomposition products. Taking into account the high rate of radical polymerisation of these monomers, it may be assumed that stabilisation of their properties will present a more complex problem than the stabilisation of acrylates and methacrylates.

IV. Properties and use of polymers

Fluorinated polymers have played a very large role in present-day technology because of their stability when used under extreme conditions.[87–89]

Studies of recent years have shown that α-fluoroacrylate polymers have many working characteristics that are significantly superior to those of their methacrylate analogues. The introduction of fluorine into the α-position relative to the acrylate ester group resulted in an improvement in the properties of block organic glass on the basis of its heat resistance and impact resistance.[21,90,91] Amongst polymers of this class poly(phenyl α-fluoroacrylate) has the best properties, so it could be recommended as a construction material for the glazing of cockpits in high-speed aircraft.[21,59,91]

In Table 8 the effect of introducing fluorine into the α-position on the heat-resistance of block acrylic homopolymers is demonstrated.

Table 8. Softening point of block homopolymers of α-substituted acrylate esters.

Monomer	T_s, °C	Refs.	Monomer	T_s, °C	Refs.
$CH_2=CHCO_2Me$	3	[73]	$CH_2=CClCO_2Me$	145	[73]
$CH_2=CHCO_2Et$	−22	[73]	$CH_2=CClCO_2Et$	94	[73]
$CH_2=CHCO_2Ph$	55	[92]	$CH_2=CFCO_2Me$	142	[73]
$CH_2=C(CH_3)CO_2Me$	120	[73]	$CH_2=CFCO_2Et$	94	[73]
$CH_2=C(CH_3)CO_2Et$	65	[92]	$CH_2=CFCO_2Ph$	180	[91]
$CH_2=C(CH_3)CO_2Ph$	110	[92]			

These data indicate that the heat resistance of polyacrylic polymers is significantly affected not only by the substituent at the α-position relative to the ester group but also by the structure of the substituent in the ester part of the molecule. Usually polar and bulky substituents increase the softening point of the polymers.[92] α-Halogenated polyacrylate esters have the greatest heat resistance, with α-chloro- and α-fluoro-acrylic polymers having the same value of T_s. However, more fundamental studies on these polymers showed that α-fluoroacrylates are very much superior to α-chloroacrylates in terms of their thermal stability (from the loss of weight at elevated temperatures).[73] Thermogravimetric analysis of poly(methyl fluoroacrylate) [poly(MFA)], poly(ethyl fluoroacrylate) [poly(EFA)], and poly(ethyl chloroacrylate) [poly(ECA)] showed that polyacrylic polymers undergo thermal depolymerisation over a narrow temperature range with a maximum rate of decomposition at 400 °C for poly(MFA) and 370° for poly(EFA). The decomposition of poly(ECA) starts at as low a temperture as 180 °C, it is a more complex process and involves not only depolymerisation but also dehydrochorination.[73] Research workers attribute the high thermal stability of α-fluoroacrylates to the greater stereoregularity of poly(α-fluoroacrylate) radicals, namely, to their higher content of isotactic diads.[73,93,94]

The high chemical stability of polymethyl and polyphenyl α-fluoroacrylates is also likely to be related to structural features.

The thermal decomposition of certain poly(α-fluoroacrylates) has been studied.[95,96] The rates of weight loss of polymers (w) when the degree of decomposition is 10% and the energy of activation of thermal decomposition (E) of poly(methyl α-fluoroacrylate) (PMFA) and poly(1,1,5-trihydrooctafluoroamyl α-fluoroacrylate) (PFAFA) correlated with their acrylate analogues—poly(methyl methacrylate) (PMMA) and poly(1,1,5-trihydrooctafluoroamyl acrylate) (PFAA)—are given in Table 9.

Table 9. Kinetic data on thermal decomposition of polymers.[95]

Polymer	$w \times 10^2$, % s^{-1} at a temperature of (°C):						E, kcal mol^{-1}
	300	310	320	330	340	350	
PMA	0.11	0.15	0.31	0.83	1.52	3.18	45.4
PMFA	0.07	0.13	0.17	0.34	0.64	1.29	50.2
PFAA	0.05	0.12	0.17	0.40	0.59	1.05	28.7
PFAFA	0.06	0.12	0.26	0.46	0.83	1.46	44.2

The data on the thermal decomposition of poly(α-fluoroacrylates) show that the latter have comparable thermal stability to that of polyacrylates that are unsubstituted at the α-position. Gorelov et al.[95,96] attribute the substantial difference in the values of the energy of activation to the different types of reactions that occur during thermal decomposition.

Further studies on poly(α-fluoroacrylates) revealed another promising area of their application—as optical materials in the priority area of the present-day technology of information communication and transmission, namely, fibre optics.[97,99–107] The outstanding optical properties of these polymers combined with their improved heat resistance, flexibility, and moisture resistance give them a considerable advantage over fluorine-containing methacrylates which have been widely studied and used in fibre optics. At the present time many new α-fluoroacrylic monomers and polymers have been synthesised and patented; they have a wide range of refractive index (1.36–1.50), so they could be used as materials for a light-guiding centre and light-reflective membrane.[99–107]

Boguslavskaya et al.[97] carried out a comparative study of the optical and physicomechanical properties of fluoroalkyl α-fluoroacrylate and methacrylate polymers. The molecular weight of block polymers are usually in the range 1 000 000–5 000 000. The properties of the polymers were correlated according to the following parameters: the transmission factor (K_{tr}), refractive index (n_D), softening point (T_s), impact strength (a_n), tensile strength at break (σ_b), specific elongation at break (ε_b), and also the thermal stability relative to visible degradation (T_{stab}). In this case the thermal stability denotes the maximum temperature at which heating a sample for 2 h does not produce any defects (bubbles, cracking, etc.). The results are given in Table 10.

Table 10. Properties of block polymers.

Monomers	K_{tr}, %	n_D^{20}	T_s, °C	a_n, kJ m^{-2}	σ_b, MPa	ε_b, %	T_{stab}	Refs.
$CH_2=CFCO_2R$								
R=Me	91	1.459	140	22	96	4.6	240	[97]
$CH_2CF_2CF_2H$	91	1.398	95	21	54	66	230	[97,99]
$CH_2(CF_2CF_2)_2H$	90	1.379	77	—	18	24	—	[97]
$CH_2CF_2CF_3$	—	1.370	105	—	—	—	—	[99]
CH_2CF_3	91	1.385	123	17	63	12.5	220	[97,99]
$C(CH_3)_2CF_2CF_2H$	90	1.400	133	—	—	—	—	[97,99]
$C(CF_2)_2CF_2CF_2CF_3$	90	1.330	60	—	—	—	—	—
$CH_2CF(CF_3)_2$	90	1.360	108	—	—	—	200	[97,99]
C_6F_5	86	1.457	174	4	56	3.1	210	[97,102]
$CH_2=C(CH_3)CO_2R$								
R=Me	90	1.491	113	10	77	3.3	180	[97]
$CH_2CF_2CF_2H$	91	1.422	71	6	47	2.7	170	[97]
$CH_2(CF_2CF_2)_2H$	91	1.400	50	—	—	—	—	[97]
$CH_2CF_2CF_3$	—	1.395	72	—	—	—	—	[108]
CH_2CF_3	91	1.416	76	7	48	2.0	180	[97,108]
$C(CF_3)CF_2CF_2CF_3$	90	1.346	62	—	—	—	—	[97]
C_6F_5	—	1.487	115	—	—	—	—	[102]

It can be seen from Table 10 that block poly(fluoroalkyl α-fluoroacrylates) with relatively short fluoroalkyl residues (1–3 carbon atoms) have considerably higher values of the softening point (more than 20 °C) and thermal stability (40–60 °C) than their methacrylate analogues. Poly(α-fluoroacrylates) are superior to their methacrylate analogues in terms of impact strength, tensile strength, and elasticity, and they have a higher level of deformation-strength properties at high temperatures.[97,108] Moreover, α-fluoroacrylic polymers are more stable towards various ageing factors (effect of heat and moisture) than the corresponding methacrylates.[97,99] In addition to fibre optics, fluoroalkyl α-fluoroacrylates can be used as materials for optical storage systems such as optical disks.[102,109]

Highly fluorinated compounds usually dissolve oxygen effectively. This property of poly(fluoroalkyl α-fluoroarylates) has been utilised when they were patented as effective gas-separation membranes[110–112] that are superior to their methacrylate analogues in terms of oxygen permeability and mechanical strength.

$$-(-CH_2-\underset{\displaystyle CO_2(CH_2)_m CFX(OCH_2CFX)_n OPr}{\underset{|}{CF}}-)-$$

X=F, fluoroalkyl (C_{1-3}); $m=1-3$; $n=0-5$.

Fluoroacrylic polymers which contain OH groups in the ester part of the molecule have been suggested as materials for contact lenses.[113,114]

$$-(-CH_2)-\underset{\displaystyle CO_2(CH_2)_m R}{\underset{|}{CF}}-)-$$

R – fluoroalkyl with OH group; $m=1-5$.

α-Fluoroacrylic polymers with improved mechanical strength have been patented as dental prosthetic materials.[115] Poly(methyl α-fluoroacrylate) can undergo decomposition when exposed to certain forms of radiation (UV, X-rays) and can be used in semiconductor technology for the manufacture of photoresistors.[74,87] Fluoroacrylic polymers can also be used in other areas of industry such as in paint production.[12,13,15]

The unique properties of polymeric α-fluoroacrylates, as is evident from the previous section of this review, when they are widely applied can give rise to substantial progress in many areas of technology and medicine.

A restriction on the application of these materials arises from the fact that so far no methods exist for preparing monomers of this class that are suitable for the development of an industrial process. Not one of the methods examined in Section II satisfies the current strict requirements for simplicity of design, safety, and ecological purity. Whilst amongst the group of traditional acrylic monomers, acrylic and methacrylic acids are the main members of the series and constitute starting materials for the synthesis of the remaining monomers, it is unlikely that α-fluoroacrylic acid could be used as a starting material for α-fluoroacrylates. In contrast to liquid acrylic and methacrylic acids, α-fluoroacrylic acid is a solid (m.p. 51 °C), so that it is extremely difficult to stabilise it against uncontrolled polymerisation. Consequently, the methods of preparation of α-fluoroacrylates are fundamentally different from those for acrylates and methacrylates, and even when produced on a small scale α-fluoroacrylates can have a considerable impact on the development of novel systems and compounds providing current technological progress. Therefore, future research into improved methods of

obtaining α-fluoroacrylic monomers, polymers, and composite materials is a promising area of organofluorine synthesis.

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Chemistry of the atmosphere and the climate

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ABSTRACT. The influence of the chemical composition of the atmosphere on the greenhouse effect and climate is analysed, and the major role of the biosphere in regulating this composition is discussed. Evidence of the observed variation trends of concentrations of small admixtures of optically active atmospheric components is presented, and the attendant possible changes in climate are outlined. A brief characterisation of the main properties of the atmospheric aerosol is given, and its role in shaping climate assessed.

The bibliography includes 26 references.

Contents

I. Introduction 920
II. Chemistry of the atmosphere and the greenhouse effect 920
III. Observed variation trends in the trace gas components in the atmosphere, and their effect on the climate 922
VI. Aerosol and the climate 924

I. Introduction

The climate and its changes are governed by the complex interaction between the components of a system composed of the atmosphere, the hydrosphere, the lithosphere, the cryosphere, and the biosphere. This system functions under conditions where solar radiation is practically the only source of energy. The atmosphere plays an important part in the development of the greenhouse effect because it contains a large number of optically active trace gaseous and aerosol components (TGAC).[1–13] Clouds are the most essential climate-forming component of the atmosphere. Their formation is associated with TGAC.[14] This fact determines the key role of chemical and photochemical processes as shapers of climate.

Information concerning the direct influence of various atmospheric chemical components on its absorption of UV radiation, the greenhouse effect, the photochemical formation of oxidants, the acidity of precipitation, and the corrosion of materials is presented in Table 1.[15] The choice of the key atmospheric phenomena is of course arbitrary and may vary according to the specific features of the problem under investigation.

It is also important to consider the large number of indirect influences (e.g. the effect of halocarbons on the ozone content, etc.). The synergism resulting from the interaction between various chemical processes in the atmosphere and biosphere should likewise be taken into account.

Table 2 shows the effect of diverse factors on the development of the chemical composition of the atmosphere.[15]

II. Chemistry of the atmosphere and the greenhouse effect

Table 3 lists the trace gas components (TGC) that exert a significant influence on the development of the greenhouse effect and related chemical processes in the atmosphere. Sixteen different characteristics of these components are presented.[12,13] The degree of reliability of available data on the sources of these components, their concentration and the variation trends for the latter, their lifetime in the atmosphere, their chemical activity, and their contribution to the greenhouse effect, has been assessed. There are still many gaps in our knowledge of the cycle of such important TGC as CH_4, CO, N_2O, and NO_x. The fact that our data on the contribution of processes connected with fossil fuel combustion (for the generation of energy) are not completely reliable, is a matter for great concern, because these contributions may account for 75% of the total anthropogenic emissions. For a clearer picture of the impact of the greenhouse effect on climate, studies of climatic chemical phenomena should be continued.

The reliability of estimates of anthropogenic influences on the chemical composition of the atmosphere, and of the environmental changes they cause is greatly limited by our inadequate knowledge of the relevant physical, chemical, and biological processes. Within a time scale of about a decade, the atmosphere, the continents and the seas represent a single system. The physical and chemical processes in the atmosphere which are subjected to increasing anthropogenic loads play a vital part in the development of biogeochemical cycles. Life on our planet depends on these cycles.

The main feature of the atmosphere is its heterogeneity. A fundamental feature of the atmosphere is its heterogeneous nature. Water in all its states plays a major role in the chemistry of the atmosphere. In particular, it is a source of hydroxyl OH (the main participant in gas-phase reactions), and of peroxide H_2O_2 (a critical oxidising agent in reactions between liquid components). Water in its liquid form (clouds and rain) has a significant effect on the chemical transformations of various compounds as well as on the tropospheric cycles of sulphur, nitrogen, carbon, halogens, and other elements. It is impossible to give an adequate description of these cycles without a detailed investigation of the processes of transformation of gas into particles and the part played by clouds and rain in these events.

Studies of the heterogeneous chemical processes in the atmosphere are of crucial importance for an understanding of the special features of the development of biogeochemical cycles. Such studies are expected to: (1) establish the relationship between homogeneous and heterogeneous processes and the rates of the gas-phase reactions; (2) establish the role of heterogeneous processes in transport phenomena, physical and chemical transformations, and washout mechanisms—all of which govern the spatiotemporal variability of the key components of the biogeochemical cycles (rain clouds,

rainless clouds, aerosols etc.); and (3) reveal the contribution of heterogeneous processes as factors responsible for changes in weather and climate.

The anthropogenic influences on climate are multiple and diverse. Without going into the subject of micro- and mesoclimate, let us discuss the global processes resulting from changes in the amount of optically active trace gas and aerosol atmospheric components that have an impact on the greenhouse effect. In this connection the problem of increasing concentrations of atmospheric CO_2 becomes important, as well as the assessment of its effect on climate.[16]

Such an estimate is necessary for: (1) predicting industrial development and its effect on the biosphere in the coming 50–100 years; (2) establishing the regularities of the global carbon cycle; (3) developing a reliable climatic theory. However, at present there are too many uncertainties for us to be able to solve these three problems. By way of example, let us consider the current state of knowledge of the carbon cycle. There are conflicting estimates of the contribution of marine and continental biota to this cycle. Research over the last 10–15 years has clearly established that there is a large number of TGAC and that their contribution to the greenhouse effect is considerable.[4] Hence it is hard to get sufficiently reliable predictions for the next 50–100 years of climatic changes due to anthropogenic factors, though there is no question of the urgent need for these.

Table 1. Effect of the chemical components of the atmosphere on its most important phenomena.[15]

Constituents	Absorption of UV radiation	Greenhouse effect	Photochemical formation of oxidants	Acidity of precipitation	Decreased visibility	Corrosion of materials
C (soot)		+			+	
CO_2		+				
CO						
CH_4		+				
C_xH_y			+		+	
NO_x			+	+	+	
N_2O		+				
NH_3/NH_4^+				+		
SO_x		+		+	+	+
H_2S						+
COS						
Organic sulphur						
Halocarbons		+				+
Other halides						
Trace constituents						+
O_3	+	+	+			+

Note. + shows that this component affects the respective phenomenon.

Atmospheric composition is largley determined by the processes occurring in the biosphere. This is why the anthropogenic influences on the biosphere that change the cycles of its various components exert a considerable influence on the climate.[17,19]

Continuous synthesis and degradation of organic matter take place in the biosphere. The chemical composition of the environment is maintained in a stable state by virtue of the closed cycles of substances in the biosphere. In the pre-industrial period with its slight anthropogenic disturbances of biospheric processes, balance of the flow of substances reached a level of ~0.01% as a result of synthesis and breakdown in the biosphere.[17] This happened because there were naturally selected correlated communities of living organisms involving a huge number of species. The anthropogenic effect resulting from the synthesis and breakdown of organic matter and industrial products causes an imbalance in the fluxes of substances. This fact calls for the immediate solution of the following fundamental ecological problems: (1) ascertaining to what extent the cycles of substances in an undisturbed atmosphere are closed; (2) determining the maximum disturbances that do not cause irreversible biospheric and environmental changes; (3) obtaining data on the current state of the biosphere and environment, particularly on the extent of closure of the cycles of substances.

Table 2. Main factors affecting the chemical composition of the amtosphere.

Constituents	Oceans and estuaries	Marshland	Crops	Wild vegetation	Domestic animals	Wild animals	Biomass combustion	Petrol combustion	Coal combustion	Industrial processes
C							+	+	+	
CO_2	+		+	+			+	+	+	
CO	+			+			+	+	+	+
CH_4		+	+	+	+	+	+			
C_xH_y	+		+	+			+			
NO_x	+		+				+	+	+	+
N_2O	+		+	+			+	+	+	
NH_3/NH_4^+		+	+	+	+	+	+		+	
SO_x								+	+	+
H_2S	+	+	+	+						
COS	+	+		+						
Organic compounds	+	+		+						
Halocarbons										+
Other halides								+	+	+
Trace constituents							+	+	+	+

Note: x means that this factor affects the content of the respective component.

An analysis of biospheric energy permitted the establishment of the distribution of energy fluxes and of biogens in organisms, depending on their size.[17] It appears that 99% of the biospherical energy flux can be attributed to organisms less than 1 cm in size. Highly closed biogeochemical cycles become feasible if less than 1% of the energy flux is utilised by organisms larger than 1 cm in size. These conclusions confirm empirical data for natural communities undisturbed by anthropogenic effects.[17]

Studies of the extent of carbon cycle closure, based on the changes in carbon isotope composition of tree growth rings, are of fundamental importance.[18] The redistribution of carbon may occur mainly between four reservoirs: atmosphere, oceans, fossil fuel, and

the biosphere. Carbon "leakage" beyond the confines of these reservoirs can be disregarded. In order to establish the changes in the carbon content of the ocean and the biosphere, it is enough to find them just for one of these two reservoirs. The changes in the second one can be calculated from the equilibrium equation (law of the conservation of matter). Oceanic carbon absorption is described by two constants. The first is determined by the physicochemical absorption resistance to changes in the total carbon content, including bicarbonates and carbonates. The second is governed by the absorption resistance to concentration changes of dissolved gaseous CO_2 alone. This latter constant corresponds to changes in biological activity.

Table 3. Influence of various trace gas components in terms of their effect on the chemical processes in the atmosphere and on global climate.[12,13]

Constituent	Effect on		
	chemical processes	climate	climato-chemical phenomena
Carbon dioxide	0	2	1
Ozone	2	2	2
Methane	2	1	1
Carbon monoxide	2	0	1
Nitrous oxide	2	1	1
NO and NO_2	2	0	1
Hydroxyl	2	0	1
Trichlorofluoromethane	2	1	1
Dichlorodifluoromethane	2	1	1
Bromochlorodifluoromethane	2	0	1
Bromotrifluoromethane	2	0	1
Sulphur dioxide	1	0	1
Carbonyl sulphide	1	0	1

Note. The following notation is used: 2, strong effect; 1, moderate effect; 0, weak effect.

Because of the buffer effect on the absorption of the main ^{12}C isotope and the absence of such an effect on the absorption of the other carbon isotopes (the Bolin–Eriksson effect), these two specific constants appear in different combinations in the balance equation.[19] This allows us to estimate two independent combinations of constants from the changes in ^{14}C and ^{13}C carbon isotopes in the growth rings. In addition, an empirical buffer factor of resistance to CO_2 penetration through the atmosphere–ocean interface is used in the calculations, and corrections are made for the ^{13}C isotope fractionating. In this case no information about processes taking place in the ocean and biosphere or about their structure is required.

According to known estimates[17–19] with a significance level above 70% the emission of carbon from land biota is greater than that caused by the combustion of fossil fuel. The seas absorb the biosphere emissions, changing in the process their biological activity. As a result, the carbon content in the biosphere as a whole, including land and sea, remains essentially unchanged. On the other hand, carbon content changes separately in the land and marine parts of the biosphere, and the atmospheric carbon fluxes that reflect these changes are considerably greater than the emission due to fossil fuel combustion.

No notice has been taken to date of the possible changes in oceanic biological activity. For this reason, it was believed that carbon emissions from land biota were lower than from fossil fuel combustion. If this factor is not taken into account, agreement with the carbon balance equation has a lower than 30% significance level. It is evident that carbon cycle studies demand a new approach to the problem of anthropogenic influences on climate.

In studies of the impact of increasing amounts of atmospheric CO_2 on climate, an effect that should raise the tropospheric and lower the stratospheric temperature, feedback mechanisms have not been sufficiently considered till now. Thus, higher tropospheric temperatures should affect the distribution of water vapour, cloud, wind, rainfall, sea ice, etc. It is by no means clear in advance what the total effect of the respective feedbacks would be: would it lead to a mutual compensation of opposite effects or to an increased CO_2 effect? The same is true for the stratosphere, where changes in temperature conditions may affect photochemical processes and lead to a redistribution of such an optically active component as ozone. We are still very far from a good understanding of the mechanism of the CO_2 effect on climate. Additionally, the atmosphere is subject to the effect of many other optically active trace gas components (e.g. nitrogen oxides, freons, etc.).[3–7] Accordingly, this calls for: (1) reliable parametrisation of the radiative properties of various gases and establishment of their priority in climate models (e.g. the climatic consequences of an increase in tropospheric ozone content should be taken into account); (2) development of atmosphere models that take into account the typical features of fields of concentration of significant low-concentration gas components; (3) long-term observations to define the trends for such components; (4) development of such photochemical blocks of climate models as would permit us to turn the concentrations of optically active trace gas components into internal variables of such models; (5) continuing laboratory investigations to specify the rates of various photochemical reactions and to enlarge the database of fine structure parameters for the absorption spectra of optically active atmospheric compounds; (6) improvement of climatic models for assessing the effect of atmospheric composition on climate by interactive consideration of oceanic processes, also in the presence of ice on the water.

III. Trends in changes of content of atmospheric trace gas components and their effect on climate

It is now generally accepted that anomalies of the radiative effect on the atmosphere due to increasing amounts of anthropogenic trace gas components (TGC) may become a dominating factor in climatic changes over several decades or longer, though there is as yet no conclusive cause and effect explanation for the changes in climate in the last 125 years.[20] Climatic changes over several decades can, for instance, be caused by the intrinsic variability of the system "atmosphere–ocean–land–cryosphere", the basis of which is the inconstancy of oceanic, sea ice and glacial heat reserves.

It was important that studies of the greenhouse TGC established that the contribution of several polyatomic TGC per molecule to the greenhouse effect was much greater than that of CO_2.[7] Thus, for instance, the contribution of freons-11 ($CFCl_3$) and -12(CF_2Cl_2) is 10^4 times greater than that of CO_2. This calls for a serious study of the part played by numerous TGC in the development of the greenhouse effect.

The results of studies of the influence of stratospheric ozone disturbances on tropospheric climate effected through the radiative-dynamic stratosphere-troposphere interaction are very important. Recent calculations also show that an increase in tropospheric content promotes development of the greenhouse effect.[7]

Computational modelling has demonstrated that should the concentrations of numerous TGC's retain their rate of increase during several future decades, the resulting rise of ground surface air temperature (GSAT) may exceed the rise in temperature observed in the last 100 years. It can cause an effect comparable to that caused by the rise in CO_2 concentration. Stratospheric changes caused by anthropogenic factors may also considerably exceed natural decennial fluctuations. In particular, calculations have established the dependence of tropical tropopause temperature on concentrations of ozone and freons.[6]

Today, first and foremost, it is necessary to study the interaction between radiative, chemical, and dynamic processes which determine in particular the ozone layer resistance to chemical factors. The "radiative-dynamic" interaction of the tropo- and stratosphere, as well as the exchange of LCGC between them are major aspects of the anthropogenic effects on climate. These problems are connected with the need to take into account stratospheric water vapour and ozone content. Observations on long term trends in the content not only of CO_2 but also of O_3, water, and of such TCGC as methane, nitrous oxide, freons, etc., are becoming increasingly urgent.

Accordingly, various aspects of the TGC effect on climate are discussed in detail.[20] Analysis of data on the greenhouse effect of TGC showed that this had grown in the last few decades at a rate 3 to 10 times higher than in 1850–1960. The cumulative balanced rise in GST due to CO_2 and other TGC after 1850 should by 1960 have reached a level of 0.7 to 2 K, the TGC contribution being about 30% (the indeterminacy being mainly due to the unreliable estimate of climatic sensitivity to radiative disturbances). Approximate calculations within the framework of a nonstationary one-dimensional model (observing diffusion in the ocean) showed that by 1980 the heating was likely to have reached 0.4–0.8 K (with the range of balanced heating equalling 0.7–2.0 K).

Calculations of heating, according to various assumptions on the temporal dynamics of TGC content, led to the conclusion that the possible GSAT rise between 1980 and 2030 will range form 0.8 to 4.1 K. Hence in 180 years (1850–2030) the cumulative heating of the system in equilibrium can reach 1.5–6.1 K. However, because of the huge thermal inertia of the seas, only 40–50% of this heating is likely to take place by 2030.

If the current growth rate for TGC remains unaltered in future decades as well, the climatic system will become increasingly unbalanced. One should keep in mind that, although several freons[10,114,115,14,13B] with a life span of ~100–500 years do not contribute appreciably to the greenhouse effect today (nor will they in the coming 50–100 years), their continued emission at the same rate might lead to considerable climatic changes in the centuries to come.

The interaction of chemical, reactive and dynamic processes in the atmosphere, as well as adequate consideration of the seas and clouds as climate-forming factors, are of special interest. So far even the sign of the cloud feedback has not been reliably established, while the assessed values for the decelerating influence of the seas range from several decades to a hundred years. As the spatial-temporal distribution of TGC is highly heterogeneous, assessment of its effect on climate in 1-dimensional models should be regarded as purely illustrative. Two- and three-dimensional models allow more reliable calculations.

Problems which should be given top priority include the following: (1) establishment of the role of chemical reactions and transport (advection, diffusion) as determinants for ozone concentration fields, as well as of nitrogen oxides and CO; (2) consideration of the temperature feedback affecting water vapour content and chemical reactions in which hydroxyl participates; (3) analysis of the contribution of biogenic sources of methane and nitrous oxide; (4) investigation of the dependence of stratospheric water vapour content on temperature at tropical tropopause level, because water vapour reaches the stratosphere mainly through breaks in the tropical tropopause.

Regular observations of TGC are becoming crucial, because the regularities of the spatiotemporal distribution of such important TGC as CO, O_3 and nitrogen oxides are still poorly understood. Direct measurement of the TGC radiative effect reflected in the special distribution of short and long wave radiation in the free atmosphere (up to the upper boundary of its optically active layer) is also unquestionably an urgent problem. Temperature changes at ground level in the tropo- and stratosphere remain an important field of study. The spectral parameters of TGC call for further investigation. Reliable evaluation of the TGC contribution to the greenhouse effect depends on their correct determination.

In order to obtain more reliable estimates of the effect of CO_2 concentrations on climate, several external climate-forming factors were analysed. These include the concentrations of TGC and tropo- and stratospheric aerosol, the solar constant, the characteristics of the underlying surface, and the volume of industrial heat release (with TGC concentration being the main factor).[11]

Table 4. Concentrations of "greenhouse" TGC and their rate of increase.[7]

Component	Concentration, p.p.m.*	Current rate of increase (%/year)
Carbon dioxide	340	0.4
Stratospheric ozone	(0.1–10)	0–0.3
Tropospheric	(0.02–0.1)	0–0.7
Methane	1.7	1.2
Carbon monoxide	0.12	?
Trichlorofluoromethane	$1.9 \cdot 10^{-4}$	5–8
Dichlorodifluoromethane	$3.5 \cdot 10^{-4}$	5–8
1,1,1-Trichloroethane	$1.3 \cdot 10^{-4}$	5–8
Freon-113	$0.3 \cdot 10^{-4}$	15–20
Carbon tetrachloride	$1.5 \cdot 10^{-4}$	1–3
Ethylene and other carbohydrates	10^{-3}	?
Nitrous oxide	0.3	0.2
Nitrogen oxides	$(3 \cdot 10^{-3}$–$0.015)$	?
Carbon disulphide	$0.3 \cdot 10^{-4}$	?
Carbonyl sulphide	$5 \cdot 10^{-4}$	?
Sulphur dioxide	$1.0 \cdot 10^{-4}$	?
Stratospheric water vapour	3–5	?

*Possible limits of changes in concentrations are shown in parentheses.

Table 4 presents current data on the values of the mixing ratio (weight fraction) for various TGC and the respective rates of increase.[7] The high rate of increase of methane concentration is very important, but the reason for this is not yet clear. It could include intensified anthropogenic emission (due to growing population, the expanding area of paddy fields, burning of vegetation, etc.), and the drop in hydroxyl concentrations (the reaction with OH is the main CH_4 sink in the atmosphere). The factors that determine the rise in nitrous oxide concentrations (combustion of fossil fuels, denitrification of fertilisers, etc.) have also not been sufficiently deeply studied. It seems that fossil fuel combustion and fertiliser denitrification are the major processes increasing the nitrogen oxide content of the lower troposphere.

Table 5. Sensitivity of ground surface air temperature (GSAT) and total ozone content to TGC concentration changes (ppm, parts per million; ppb, parts per billion).

Component	Change in TGC concentration	Change in GSAT, °C	Change in total ozone, %
CO_2	330→600 p.p.m.	1.5–4.5	3.1
Methane	1.7→3.4 p.p.m.	0.2–0.4	2.1–3.3
Chlorocarbons	0→1.0 p.p.b. ($CFCl_3$)*	0.5	−3.3 to −5.5
	0→2.7 p.p.b. (CF_2Cl_2)*		
	0→1.8 p.p.b. ($CFCl_3$)**	1.0	−15.7
	0→5.0 p.p.b. (CF_2Cl_2)**		
	0→1.5 p.p.b. (CH_3CCl_3)**		
Nitrous oxide	0.3→0.6 p.p.m.	0.3–0.4	−8.7 to −10.7
Ozone	doubling of tropospheric concentration	0.9	
Water	3–6 p.p.m. in stratosphere	0.6	

*Steady emissions at 1977 level.
**Doubled steady emissions at 1983 level.

The TCG effect on climate has three known mechanisms: (1) direct radiative action; (2) climatochemical interaction (TCG-created changes in atmospheric chemical composition); (3) dynamics-dependent feedback. Table 5 contains data on the effect of rises in concentration of various TGC on globally averaged values for ground surface air temperatures (GSAT) and on ozone concentration. This evidence was obtained on one-dimensional models.[7] In computer climate modelling, the influence of the tropospheric aerosol is not as a rule considered. However, it should be remembered that it could increase the amount of solar radiation reaching the Earth by 5 W m^{-2}. This is comparable to the effect of doubled CO_2 concentrations. The considerable uncertainty seen in the evaluation of anthropogenic effects on climate is due to the absence of reliable data on the parameters of cloud formation.

Table 6 shows how high the GSAT may rise under the influence of CO_2 and other TGS.[11] Calculations were carried out at predetermined values for relative humidity, the height of the top cloud edge, and the ice cover albedo. A similar study is described in Ref. 2.

Table 6. Possible rise in ground surface air temperature (GSAT) due to CO_2 and other TGC.[11]

Component	GSAT rise, °C	
	1950–1980	1980–2010
CO_2	0.25	0.39
$CO_2+NO_x+CH_4+NO_2+O_3+$ chlorocarbons	0.50	0.80

IV. Aerosol and climate

The atmospheric aerosol is a product of a complicated set of chemical and physical processes. Because these processes are so complex, and the life of the aerosol is relatively short, the chemical and physical characteristics of the latter are highly variable.[4] This variability is so great and the observational data are so fragmentary, that so far it has proved impossible to make a sufficiently reliable estimate of the total balance of different types of aerosol. The available estimates of the strength of the global sources of natural and anthropogenic aerosol are purely tentative.

However, there is no doubt that the estimates for anthropogenic aerosol are the more reliable (it is especially difficult to assess natural aerosol concentrations over inaccessible parts of the ocean and the continents). This is the reason for the low reliability of data on natural/anthropogenic aerosol ratios, though on a global scale the effect of man's economic activity on the sulphur and nitrogen cycles can be clearly seen.

Depending on composition and sources, one can classify natural aerosols as follows: (1) products of sea spray evaporation; (2) mineral dust carried into the atmosphere by wind; (3) volcanic aerosols (both directly emitted into the atmosphere and resulting from gas-phase reactions); (4) particles of biogenic origin (again, both directly emitted or the product of gas-phase reactions); (5) smoke from biota combustion on land; (6) products of natural gas-phase reactions (e.g. sulphates formed by the oxidation of sulphur derived from the ocean surface).

Similarly, there are several types of anthropogenic aerosols: (1) direct industrial emissions (e.g. particles of soot, smoke, and road dust, etc.); (2) products of gas-phase reactions. Besides that, we should distinguish tropospheric and stratospheric (mainly volcanic) aerosols. Aerosols may be formed in gas-phase reactions as a result of the following processes: (1) homogeneous homomolecular nucleation (formation of tiny new liquid or solid stable particles in the gas phase in the presence of only one gaseous component); (2) homogeneous heteromolecular nucleation (a similar process but with two or more gases participating); (3) heterogeneous heteromolecular condensation (already formed particles increasing in size due to gas adsorption).

The photochemical reactions responsible for the initial transformation of the "highly volatile" gas into a gas component which becomes a source of aerosol formation are very complex and as yet have been poorly described. The following processes appear to be the most important: (1) reactions of sulphur dioxide with hydroxyl radicals which lead to the formation of molecules of sulphuric acid and sulphuric aerosol; (2) reactions between non-methane hydrocarbons and ozone and/or hydroxyl radicals. As a

result, aldehydes, alcohols, carbonic and dicarbonic acids are formed (as a rule the secondary products of these reactions interact with nitrogen oxides, forming organic nitrates). Ozone and HO and HO_2 radicals play a very important part in atmospheric chemistry. These radicals are either direct or indirect products of photochemical reactions (this is why the gas-phase processes resulting in particle formation are usually highy dependent on daylight.

Organic particles are some of the most important types of atmospheric aerosols. Because the organic compounds emitted into the atmosphere are so diverse and participate in so many reactions, it is extremely difficult to study them. The concentration of soot particles is very high. Over oceans it reaches mean values of about 0.5 $\mu g\ m^{-3}$, which is comparable with mineral aerosol concentrations. It seems that the origin of the organic aerosol is half natural and half anthropogenic. The ocean accounts for about half of the natural aerosol.

As a rule, the effect of aerosol on various processes is determined by a whole combination of chemical and physical processes. These are significantly influenced by the size of the aerosol particles. In order to obtain an adequate description of a real aerosol, it is necessary to carry out a comprehensive appraisal of its various characteristics. In most cases it is the mass concentration of the aerosol that is determined. But this characteristic is usually the least informative one, because it carries no information about the sources, composition and possible effects of the aerosol.

Aerosol cycles are closely connected with moisture transformation in the atmosphere: clouds and rain play an important part in the formation and transformation of the aerosol and its removal from the atmosphere. The aerosol in its turn has a significant effect on microphysical processes in the clouds. It is not just a coincidence that the life of the aerosol in the lower and upper troposphere is one to two weeks, while that of water vapour is ten days. It is impossible to have a full understanding of the processes of aerosol formation and transformation without reliable data on cloud physics and chemistry. For this reason, studies of the nucleation mechanism are extremely important.

There is good reason to fear that the increase in anthropogenic aerosol content may affect the climate by altering both the global radiation regime and the hydrological cycle. Though there is much evidence that natural and anthropogenic aerosol is dispersed to great distances from its source, there are still no reliable data to confirm the connection between man's economic activity and the trend of the global aerosol content to increase. The great spatiotemporal variability of the aerosol makes it difficult to isolate the anthropogenic component. This would become feasible only after the cause of this variability has been established. But for this an extensive programme of combined studies of the atmospheric aerosol would have to be carried out.

The aerosol affects climate mainly through its influence on the transmission of short and long wavelength radiation. Besides that, climatic changes can induce regional and global alterations in the content and composition of atmospheric aerosols.[4] In addition to the direct radiative effects, one should also take into account the indirect effects, e.g. the effects that are connected with changes in the microphysical characteristics of clouds. The great variability of the spatial distribution and properties of aerosols from different sources (wind erosion of soil, volcanic eruptions, sea foam, forest fires, biospheric and anthropogenic sources, gas-phase reactions, etc.) and shortage of data prevent us from obtaining a reliable picture of aerosol distribution over the globe. The optical properties of the aerosol depend on its concentration, its microstructure, and the complex refractive index.

It is convenient to use four parameters in examining the radiative effects of the aerosol: the relationship between the absorption strength of the particles in the short wavelength radiation range and backward scattering, the long wavelength radiative strength, underlying surface albedo, and the height of the sun. Priority should be given to the following objectives: (1) development of realistic aerosol models suitable for studying climatic sensitivity to aerosol effects; (2) development of parametric models for radiation transmission and the assessment of the radiative effect of aerosols in the above models; (3) application of the parametric models in climatic models in order to evaluate radiative effects; (4) development of the means for obtaining global information on aerosols (recommended for this reason it is that a draft programme for global aerosol monitoring be prepared).

It is especially important for us to study volcanic aerosols, because volcanic eruptions can be regarded as a natural "experiment" that allows us to really test models for the study of climatic effects.[6,7,9,10] Accordingly, it is important that a special international programme of observation, ready for implementation at the next big eruption, should be prepared. This would allow us to obtain comprehensive documentation of the climatic consequences of the eruption and other associated phenomena.

It is only very recently that the first attempts were made to use complicated three-dimensional climatic models to assess the climate-forming role of aerosols. The study by Coaxley and Cass is an interesting example of such computer modelling of the climate.[21]

Usually, the natural tropospheric background aerosol is not taken into account in computer modelling of the general atmospheric circulation (GAC). However, calculations show that the aerosol causes a reduction by 5.0 $W\ m^{-2}$ in the short wavelength radiation balance at the underlying surface level and one of 3.5 $W\ m^{-2}$ at the top of the atmosphere. This means that it creates radiation disturbances of about the same magnitude (but with the opposite sign) as doubling of CO_2 concentration (one should of course also take into account the effect of aerosol on the heat radiation field).

In contrast to the relatively homogeneous global radiative disturbances caused by CO_2, aerosol has a spatially heterogeneous effect on the radiation regime. This is connected with the spatial variability of the aerosol content and the underlying surface albedo, as well as with the varying height of the sun above the horizon. Calculations of climatic sensitivity to the effect of aerosol were carried out on a GAC model developed at the National Centre for Atmospheric Research, USA (NCAR). Present disturbances of short wavelength radiative heat flux similar to that received in July was initially introduced into the model.[21] The distribution of snow cover, sea ice, and ocean surface temperature (OST) were also fixed, as was the sun's height.

As the OST distribution in this model is rigidly fixed, the aerosol should have a weak effect on the temperature field. Special attention was given to isolating the weak aerosol signal from the intrinsic climatic background variability common for this model. An aerosol-created radiative disturbnce equivalent to the above mentioned 1.5 $W\ m^{-2}$ increase in the radiation absorbed by the atmosphere was introduced on the (arbitrary) 201st day of integration. Subsequently it lasted up to 600 days (the same period as the control experiment with no aerosol). An analysis of the averaged results for seven thirty-day intervals from the last 350 arbitrary days was carried out: these intervals were divided by

20-day breaks to ensure the statistical independence of the averaged results.

Examination of the averaged meridional profile of the surface temperature shows that there is a general cooling with local subarctic warming. The aerosol-induced large scale cooling can be considered statistically significant. The average global temperature drop is 0.08 K (with fixed OST this corresponds to a drop of 0.32 K). Computation of the average vertical temperature profile for the northern hemisphere points to a cooling of the whole thickness of the atmosphere. A statistically significant (90% confidence level) cooling of the lower troposphere (1000–500 hPa) amounted to 0.17 K. Computation of the surface temperature on the basis of the energy-balance climate model (EBCM) shows that the changes should be greater by an order of magnitude. This discrepancy can be attributed, first, to the fact that the EBCM takes the albedo feedback into account; second, that it deals with average annual conditions; and third, that it assumes that an equilibrium has been achieved. In a GAC model the latter depends to a great extent on the preset OST.[7] The internal variability of the model itself is extremely important. Without it, errors may arise which will impart to the aerosol effect a wrong sign.[21]

The effect of the atmospheric aerosol (in all its various types) on the development of the temperature field can be assessed with the help of a 15-level global spectral model of the climate (which deals with wavenumbers up to 15). It was developed at the European Centre for Medium Range Weather Forecasting (ECMWF).[22] Fifteen series of integrations over a 90-day period with averaging of the last 30 days (summer weather conditions) at fixed ocean surface temperatures were carried out. Eight of the series were used to evaluate the aerosol effect in different seasons.

Table 7. Optical parameters specific to various types of aerosol.[4]

Type of aerosol	$\tilde{w}_0$ (0.55 μm)	$1-g$	$\tilde{w}_0$ (10 μm)	$\frac{\sigma_e\ (10\ \mu m)}{\sigma_e\ (0.55\ \mu m)}$
Soot	0.209	0.66	0	0.038
Oceanic	1	0.22	0.692	0.250
Dust	0.653	0.12	0.558	1.08
Water soluble	0.957	0.37	0.209	0.019
Marine	0.989	0.26	0.680	0.19
Continental	0.891	0.36	0.486	0.097
Urban	0.647	0.41	0.173	0.033
Sulphuric acid (75% H_2SO_4)	1	0.27	0.010	0.050
Volcanic	0.947	0.30	0.130	0.035

An analysis of the zone-averaged temperature fields indicates that the induced heating of the stratosphere by about 2 K due to the presence of the aerosol is compensated by greater cooling at long wavelengths. This means that in conditions of a stratospheric disturbance, radiative equilibrium is restored. At the same time, in the troposphere (and first of all near the underlying surface) the heating caused by absorption of short wavelength radiation by the aerosol is balanced mainly by nonradiative factors (IR-cooling reduced the heating only by about a quarter). As a result, there is no significant change of the temperature field. The higher the location of the aerosol, the greater its effect.

Two geographical features are typical of the aerosol effect during all four seasons. One is that desert aerosol reduces net radiation. In the Sahara desert and on the Arabian peninsula the net radiation decrease amounts to 60 W m^{-2}. This leads to an appreciable drop in ground surface temperature (up to 3 K near a 20°N., 30°W. location). The other feature that becomes evident in the field of disappearing long wavelength radiation is the reduction of cloud cover in the strip from the north-eastern coast of Brazil to Texas. The maximum reduction of cloud cover observed near 15°N., 50°W. location amounted to 0.1 and caused an abnormal increase in radiation.

A rough averaged estimate gives the following values for aerosol-induced changes in the radiation regime:[1] transmitted long wavelength radiation, 0; global albedo, +0.0075; absorbed short wavelength radiation, −3.5 W m^{-2}; radiation from the ground, −1.5 W m^{-2}; total radiation, −8.5 W m^{-2}; cloud cover −0.007; terrestrial surface temperature, −0.3 K; average ambient temperature, +0.5 K.

The other 7 computer modelling series of the abovementioned 15 were used for evaluating the contributions of 7 different types of aerosol (summer weather conditions). For this purpose, one (arbitrarily chosen) type of aerosol was excluded from the computation in each series. Computations revealed the well defined nonlinear nature of the interaction between different contributions. The sum of the effects differs considerably from the effect of the sum (sometimes even the sign changes). If one compares the overall effect of all types of aerosols with the effect of a single type one can see that the closest parallelism is observed in the case of the stratospheric aerosol. The background tropospheric aerosol takes second place. The stratospheric aerosol inhibits to some degree the Hadley circulation, and also slows down the zonal air transfer in the tropical and subtropical upper troposphere.

Further studies of the atmospheric aerosol and its impact on climate should develop along the following main lines:[23] (1) effect of aerosol on climate; (2) influence of aerosol on long distance observation from satellites of climatic parameters; (3) properties of aerosols; (4) climatology of aerosols; (5) consideration of aerosol in the modelling of climate. Investigation of the climate-forming role of aerosol includes four main objectives: observation of the spatiotemporal variability of the content and properties of the tropospheric and stratospheric aerosol; development of realistic aerosol-radiation models suitable for computer climate modelling; consideration of affects of aerosol in the theory of climate; study of the interdependence between aerosol content and various climate-forming processes (land transformation, glaciation, etc.) for the purpose of developing models that would take interactive account of the presence of aerosol.

The following basic characteristics determine the influence of the aerosol on radiation transmission and its corresponding effect on climate: the bulk extinction coefficient σ_e (data on the vertical profile of σ_e allow us to calculate the optical thickness of the atmosphere τ), the bulk scattering coefficient σ_s (or the albedo of a single scattering $\tilde{\omega}_0 = \sigma_s/\sigma_e$) and the bulk scattering indicatrix. The latter can be approximately described by introducing the indicatrix asymmetry coefficient g. The ratio of the optical thickness in the 8–12 μm transparency window to the averaged optical thickness for the visible range of the spectrum is an important parameter. Some of these parameters for various types of aerosols that conform to the standard atmospheric radiation model developed by the International Radiation Committee are listed in Table 7.[4]

Assessment of the effect of aerosol on climate is reduced in most cases to computation of the influence of the aerosol parameters on the global radiation balance (GRB) and the temperature of the ground surface. Changes in GRB are mainly determined by the albedo variation of the "ground surface–atmosphere" system. In a cloudless atmosphere, the sign of the change in the albedo of the system (increase or decrease) is determined by the content and optical properties of the aerosol (in the first place by the single-scattering albedo), the underlying surface albedo, and the height of the sun. It would appear that, overall, there is a decrease of the overall GRB because of the aerosol-induced increase of the albedo.

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The chemistry of OH and HO_2 radicals in the earth's atmosphere

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ABSTRACT. In the present review the main photochemical mechanisms for reaction of OH and HO_2 with atmospheric components are examined and possible alternative methods of studying them are analysed. The mechanisms governing the change in concentrations of OH and HO_2 radicals cannot be represented without a consideration of other stable and labile minor gas components in the atmosphere. Amongst the latter the most important are ozone, ozone-active radicals and their precursors, stable molecules. In addition to OH and HO_2, NO, NO_2, as well as Cl and ClO are also reactive towards ozone. The destruction cycles for ozone involving these radicals and reactions related to them are also briefly examined in this review together with the heterogeneous processes involving OH and HO_2 that can also substantially affect the gaseous composition of the atmosphere.

The bibliography includes 72 references.

Contents

I. Introduction 928
II. The atmosphere as a multicomponent chemical system 928
III. Photochemical balance between OH, HO_2, and ozone in the stratosphere 931
IV. Reactions of OH and HO_2 in the troposphere and oxidation of hydrocarbons. Tropospheric ozone 934
V. Effect of heterogeneous reactions on the gaseous composition of the troposphere and stratosphere 937

I. Introduction

Atmospheric photochemistry was only recognised and started to develop as an independent branch of chemistry in the middle of the 1970s, although the basic principles of the photochemical theory of the atmosphere had been formulated more than half a century ago.[1,2] This was assisted in many respects by the rapid development of technique for measuring rate constants of fundamental chemical and photochemical processes and of numerical methods for simulating the kinetics of multicomponent chemical systems using computer technology. By using the experience gained in solving kinetic problems in plasma chemistry and photochemistry and also in the calculations of different processes in chemical reactors, it was possible to achieve real progress in the understanding of the nature of chemical processes in the atmosphere and to develop the idea of it as a multicomponent non-equilibrium chemical system. The photochemical models developed from this concept made it possible to predict the gaseous composition of the atmosphere containing many chemical compounds as minor components, which was subsequently confirmed in full-scale experiments. The rapid development of studies in the field of atmospheric chemistry has recently led to its having a reverse effect on traditional areas of chemistry, which has manifested itself in particular in the revision of a whole series of kinetic data of fundamental significance for the representation of photochemical processes in the atmosphere and the development of new experimental methods for measuring rate constants of reactions involving minor gas components.

Although the present-day chemistry of the atmosphere makes use of dozens of molecular and ion-molecule reactions, photodissociation and photoionisation reactions, a special place is occupied amongst them by processes involving OH and HO_2 radicals, which because of their high chemical activity are initiators of a whole range of oxidative reactions in different regions of the atmosphere. The existing theoretical and experimental results provide convincing evidence of the key role of hydrogen radicals in a whole set of problems in atmospheric chemistry. In the lower atmosphere (troposphere) hydroxyl initiates the oxidation of CO, CH_4, C_2H_6, H_2, CH_3Cl, CH_3CCl_3, CH_3Br, H_2S, SO_2, and a number of other components of natural and anthropogenic origin. In the upper atmosphere (stratosphere and mesosphere) reactions involving OH and HO_2 are responsible for changes in the ozone content. Moreover, many questions related to a determination of the strength of atmospheric photochemical sources and sinks of OH and HO_2 and their content in the atmosphere have given rise to considerable controversy.

II. The atmosphere as a multicomponent chemical system

The earth's atmosphere contains a large number of chemical compounds, of which N_2 and O_2 are the most abundant. An important role in atmospheric photochemistry is played by the so-called precursor gases—N_2O, H_2O, CH_4, and freons of natural and anthropogenic origin. When they are oxidised in the lower atmosphere and undergo photodissociation or react with photolysis products in the upper atmosphere, these gases become sources of free radicals and other minor gas components. The content of some of the most important components at different altitudes and their sources are shown in Table 1. More detailed information about the vertical and latitudinal distribution of the minor gas components, their time variations, and determination of the total strengths of their sources can be found in two reviews.[6,7]

In restricting the discussion solely to the neutral components, we shall examine the key channels of photochemical transformation of the gas precursors.

1. Oxygen components

The photodissociation of O_2 results in the formation of atomic oxygen in the ground (^3P) and excited (^1D) states

$$O_2+h\nu\rightarrow O(^1D)+O(^3P),\ (135\ \text{nm} < \lambda < 175\ \text{nm}), \quad (1)$$

$$O_2+h\nu\rightarrow 2O(^3P),\ (175\ \text{nm} < \lambda < 250\ \text{nm}). \quad (2)$$

Ozone is formed as a result of the termolecular reaction

$$O+O_2+M\rightarrow O_3+M, \quad (3)$$

where M are air molecules.

Table 1. Some properties of the most important minor components of the atmosphere.

Gas	Background concentration, mole fractions		Extent of study of global distribution	Main sources	Main sinks
	T	S			
CH_4	$1.6\cdot10^{-6}$	$(15-6)\cdot10^{-7}$	++	B	P
N_2O	$3.2\cdot10^{-7}$	$3\cdot10^{-7}\div3\cdot10^{-10}$	++	B	P
O_3	$(4\div10)\cdot10^{-8}$	$(1\div10)\cdot10^{-6}$	+++	P	P
NO_x	$(4\div10)\cdot10^{-11}$	$1\cdot10^{-10}\div3\cdot10^{-8}$	+++(T), ++(S)	A, P storms	P, W (T)
HNO_3	$(2\div10)\cdot10^{-10}$	$8\cdot10^{-9}\div1\cdot10^{-10}$	++	P	P, W(T)
OH	$1\cdot10^{-13}\div1\cdot10^{-14}$	$3\cdot10^{-13}\div8\cdot10^{-10}$	+	P	P
HO_2	$1\cdot10^{-11}\div1\cdot10^{-14}$	$1\cdot10^{-12}\div6\cdot10^{-10}$	+	P	P
H_2O_2	$1\cdot10^{-9}\div5\cdot10^{-10}$	$1\cdot10^{-12}\div5\cdot10^{-10}$	o	P	P, W (T)
H_2CO	$4\cdot10^{-10}\div2\cdot10^{-11}$	$1\cdot10^{-11}\div1\cdot10^{-10}$	+	P	P
H_2	$5.7\cdot10^{-7}$	$5\cdot10^{-7}\div1\cdot10^{-8}$	++	B, P	P
H_2O	$1\cdot10^{-2}\div2\cdot10^{-5}$	$(1\div6)\cdot10^{-6}$	+++(T), ++(S)	H	W (T), P (S)
CO	$(2\div8)\cdot10^{-8}$	$(0.2\div10)\cdot10^{-8}$	++	A, P	P

Note. The concentrations of minor components are annual average globally mean values and are given mainly from the results of one-dimensional simulation[3] and from the data of four studies.[4-7] Conventional notation: T = troposphere, S = stratosphere, A = anthropogenic, W = rainout, P = photochemical, B = biogenic, o = no reliable measurements, + = individual measurements carried out, ++ = special series of measurements carried out, +++ = regular inspection made, NO_x = NO + NO_2, H = hydrosphere.

Oxygen atoms are consumed in the reactions

$$O+O+M\rightarrow O_2+M, \quad (4)$$

$$O+O_3\rightarrow 2O_2. \quad (5)$$

On photodissociation of ozone, oxygen atoms are again formed in their ground or excited states:

$$O_3+h\nu\rightarrow O_2+O(^3P),\ (\lambda > 320\ \text{nm}), \quad (6)$$

$$O_3+h\nu\rightarrow O_2+O(^1D),\ (\lambda < 310\ \text{nm}). \quad (7)$$

This reaction sequence, proposed by Chapman[1,2] was for a long time considered to be the main route for formation of atmospheric ozone. The sequence of stages (1)–(7) represents a chain reaction for conversion of "odd" oxygen—O and O_3—and it is sometimes called the "odd" oxygen cycle.

2. Sources of OH and HO_2

The reaction of an excited oxygen atom with a water molecule was first regarded as a photochemical source of hydroxyl by Nicolet and Bates.[8,9]

$$H_2O+O(^1D)\rightarrow OH+OH. \quad (8)$$

The formation of OH is also possible in a number of other reactions of $O(^1D)$ with minor atmospheric components:

$$CH_4+O(^1D)\rightarrow CH_3+OH, \quad (9)$$

$$H_2+O(^1D)\rightarrow H+OH. \quad (10)$$

OH and HO_2 are interconverted in reactions involving oxygen species:

$$O_3+OH\rightarrow HO_2+O_2, \quad (11)$$

$$O+HO_2\rightarrow OH+O_2. \quad (12)$$

3. Sources of nitrogen oxides

According to Crutzen[10] the following reaction represents a photochemical source of nitric oxide in the atmosphere:

$$N_2O+O(^1D)\rightarrow 2NO. \quad (13)$$

The concentration of N_2O—a product of the activity of bacteria under anaerobic conditions—rapidly decreases with altitude, ranging from 10^{12} cm^{-3} on the earth's surface to 10^8 cm^{-3} at an altitude of 35–40 km (see Table 1). A photochemical equilibrium in the system NO–NO_2 with a typical time of several tens of seconds[6] is established in the atmosphere, being determined mainly by the following reactions:

$$NO+O_3\rightarrow NO_2+O_2, \quad (14)$$

$$NO_2+O\rightarrow NO+O_2, \quad (15)$$

$$NO_2+h\nu\rightarrow NO+O. \quad (16)$$

The photochemistry of the minor gas components, taking into account the specific nature of reactions in different regions of the atmosphere, will be examined in greater detail in subsequent sections.

4. Main cycles of destruction of ozone

One of the principal problems of atmospheric chemistry is the effect of photochemical processes on the protective layer of ozone. It is evident that with the concentrations of ozone that actually exist in the stratosphere, being several orders higher than the concentration of components that are chemically active towards them (see Table 1), the destruction of ozone may be due solely to catalytic cycles of the type

$$\begin{array}{l} X + O_3 \rightarrow XO + O_2, \\ XO + O \rightarrow X + O_2, \\ \hline O_3 + O \rightarrow O_2 + O_2, \end{array} \quad (17)$$

or

$$\begin{array}{l} X + O_3 \rightarrow XO + O_2, \\ XO + O_3 \rightarrow X + 2\,O_2, \\ \hline 2\,O_3 \rightarrow 3\,O_2, \end{array} \quad (18)$$

where X = OH, NO, or a chlorine atom which is formed in the

stratosphere by photodissociation of freons. The cycles of ozone destruction involving OH, NO, and Cl are known as the hydrogen, nitrogen, and chlorine cycles respectively. Bromine atoms are also highly effective, but they are present in the atmosphere to a much lesser extent than Cl atoms. A large number of studies have been devoted to stratospheric cycles of ozone destruction, amongst which the two fundamental publications of Johnston[11,12] can be given special mention. The efficiency of action of a catalyst molecule in destruction cycles is determined by the concentration of catalyst in the atmosphere, which depends on the rates of its generation and removal from the cycle.[13] The ratio of the rate of destruction of odd oxygen to the rate of removal of catalyst from the cycle represents the chain length and corresponds to the number of O and O_3 molecules destroyed by a single catalyst molecule. The number of recurrences in the cycle can reach 10^6. In the stratosphere the nitrogen, hydrogen, and chlorine cycles (in order of increasing contribution) are active. Terminations of the chains in the cycles occur as a result of a cross interaction of the homogeneous catalysts between each other

$$OH+HO_2 \rightarrow H_2O+O_2,$$

$$OH+NO_2+M \rightarrow HNO_3+M,$$

$$ClO+NO_2+M \rightarrow ClONO_2+M$$

or as a result of the heterogeneous destruction of radicals or reservoir gases (HNO_3, $ClONO_2$) on aerosols and water droplets. However, in a number of cases termination is governed not by chemical reactions but by a process of turbulent transfer, resulting in the removal of the catalyst molecule from the stratosphere. Thus, dynamic processes affect the length of the cycles and prove to be an additional important factor that is necessary to take into consideration in simulating the gaseous composition of the atmosphere.

5. Models of the atmosphere

In photochemical models of the atmosphere use is made of a system of non-stationary diffusion kinetic equations of continuity that generally take the following form:

$$\frac{\partial [n_i]}{\partial t} = P_i - L_i [n_i] - \sum_j \frac{\partial F_{ij}}{\partial x_j}. \qquad (19)$$

Here $[n_i]$ is the concentration of the ith component, P_i and L_i are its photochemical sources and sinks respectively, x_j are Cartesian coordinates, F_{ij} are component fluxes, and t is time. In one-dimensional models, which are the most widely used, only the vertical flux component is considered

$$F_{iz} = K_z [M] \frac{\partial}{\partial z} \left(\frac{[n_i]}{[M]} \right) \qquad (20)$$

where K_z is the globally averaged vertical component of the tensor of the coefficient of diffusion transfer (turbulent or molecular), [M] is the total concentration of air molecules. In the solution of certain problems and at a given ratio between the lifetime in photochemical reactions $\tau_{chem} = 1/L_i$ and the characteristic time of dynamic transfer $\tau_{dyn} = H^2/K_z$, the equation system (19) can be simplified ($H = RT/mg$, the height of uniform atmosphere, R is the gas constant, m is the molecular weight, and g is the acceleration due to gravity).

Quasi-stationary conditions (diagnostic problem), $\partial[n_i]/\partial t = 0$. For long-lived components ($\tau_{dyn} \ll \tau_{chem}$) the system of equations in (19) takes the following form:

$$P_i - L_i [n_i] - \frac{\partial F_{iz}}{\partial z} = 0. \qquad (21)$$

In the case of short-lived components ($\tau_{chem} \ll \tau_{dyn}$) the following photochemical equilibrium is established:

$$P_i - L_i [n_i] = 0. \qquad (22)$$

Within the framework of the diagnostic problem the photochemical balance between the minor gas components is calculated in given regions of the atmosphere and the sensitivity of the equilibrium model concentrations to different perturbation mechanisms and the internal parameters of the model is determined.

Non-equilibrium conditions (prognostic problem). The whole equation system (19) is solved in this case for long-lived components, while in equations for short-lived components the transport term $\partial F_{iz}/\partial z$ can be omitted. The solution of the prognostic problem makes it possible to study the mechanism of the relaxation of the system to equilibrium conditions and to simulate the change in concentration of the minor gas components under atmospheric conditions and to predict the chemical composition in air in the atmosphere at different moments in time.

The relationship between the dynamic and photochemical lifetimes in the atmosphere is relative in nature, since the clearly defined non-uniformity of the atmosphere causes considerable changes (by several orders of magnitude) in τ_{chem} and τ_{dyn}. This factor considerably complicates a numerical solution of system (19), since the retention of the transport component on its right-hand side results in the need to solve a system of second-order partial differential equations when there is a close relationship between the equations because of the high rates of the chemical reactions.

In current photochemical models of the atmosphere, adaptation of the numerical algorithms of system (19) to include transport is considered to be one of the most complex and topical problems. Elucidation of this problem is outside the scope of the present review, but the details can be obtained from four studies.[14–17] Moreover, the need to overcome the difficulties in the calculations had led to the development of a new approach to the analysis of the photochemical parts of the model equations — the application of the concept of families.

This idea involves separating from the whole collection of components included in the scheme of reactions individual groups (families), within which the conditions of photochemical equilibrium are assumed to be fulfilled, whereas dynamic transfer is calculated for the complete family as a whole. This makes it possible to simplify considerably the numerical solution of system (19), having reduced the number of complete equations. In most photochemical models of the atmosphere the following families are usually distinguished: "odd" oxygen $O_y = O(^3P) + O(^1D) + O_3$, "odd" nitrogen $NO_y = N + NO + NO_2 + 2N_2O_5 + HO_2NO_2 + NO_3 + ClONO_2$, "odd" hydrogen $HO_y = H + OH + HO_2 + 2H_2O_2$, and "odd" chlorine $Cl_y = Cl + ClO + HOCl + ClONO_2$. The combination of components on the right sides can be modified according to the choice of reaction scheme and the atmospheric conditions under which they occur. The altitude profiles of the interconversion times for components within a single family [$OH \longleftrightarrow HO_2$ (*1*), $NO \longleftrightarrow NO_2$ (*2*)], the lifetimes of OH radicals (*3*) and families HO_y (*4*) and NO_y (*5*), the conversion time of $HNO_3 \longleftrightarrow NO_y$ (*6*),

and the lifetimes of the chemically inactive gases H_2O and CH_4 are presented in Fig. 1. The high rate of interconversion of the species of the HO_y and NO_y families and the marked difference between the lifetimes of active species and stable gases can clearly be seen in Fig. 1.

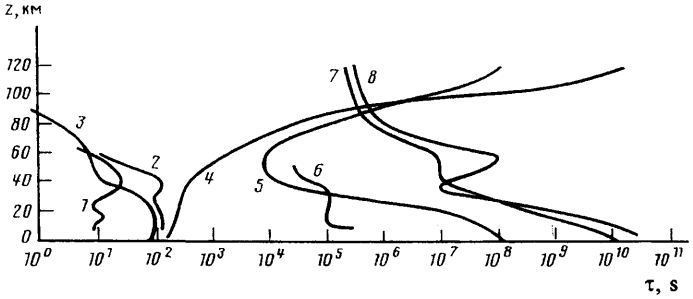


Figure 1. Lifetimes of components of the photochemical reactions of OH (*3*), NO_y (*5*), HO_y (*4*) and the gas precursors CH_4 (*8*) and H_2O (*7*), and also the time for reaching photochemical equilibrium in the systems OH/HO_2 (*1*), NO/NO_2 (*2*), and HNO_3/NO_y (*6*).[6,18]

A distinctive feature of the atmosphere as a medium for photochemical processes is the presence in it of a number of vertically divided regions, each of which is characterised by well-defined specific chemical and physical properties. The lowest region of the atmosphere—the troposphere (up to 12–15 km in altitude)—is characterised by the presence of a considerable amount of water in different aggregate states and an active lower boundary. In photochemical terms this denotes, firstly, the existence of intense heterogeneous reactions involving water droplets, aerosol particles and the earth's surface and, secondly, a greater variability of the chemical composition compared to other regions of the atmosphere as a result of the entry of anthropogenic and natural gases from the lower boundary. In this sense the troposphere may be regarded as a type of filter that limits the transfer of chemically active and water-soluble gas components into the upper layers of the atmosphere.

The stratosphere is considerably less susceptible to the effect of terrestrial sources. The only exception to this is nitrous oxide, from which nitric oxide is formed according to reaction (13), and the "odd" chlorine family, since N_2O and freons, which are inert in the troposphere, are vigorously decomposed in the stratosphere by solar UV radiation. The principal minor gas components O_3, NO, NO_2, OH, HO_2, etc. have only internal photochemical sources in the stratosphere. Also, the stratosphere is quite dry, the relative water vapour content amounting to 10^{-6} and being subject to much smaller variations than in the troposphere. The background concentration of aerosol particles in this region is also small (no more than 20–30 particles per cm^3 in a local maximum—the Junge layer—at an altitude of 16–18 km). All this makes it possible to simulate photochemical processes occurring in the stratosphere in the gas phase, and the stratosphere is characterised as the most favourable region for detailed comparison of theoretical schemes with the results of full-scale observations.

In the upper region of the atmosphere (an altitude range of 50–120 km) the role of photodissociation and photoionisation reactions increases, which helps to increase the concentrations of the atomic components of radicals and causes the formation of excited and ionised molecules and atoms. However, a leading role in the photochemistry of the neutral component of the mesosphere and lower thermosphere is played by OH and HO_2 radicals, which to a considerable extent control the content of components such as O and O_3.

III. Photochemical balance between OH, HO_2, and ozone in the stratosphere

The magnitudes of different sources and sinks of radicals of the hydrogen family are shown in Figs. 2 and 3.

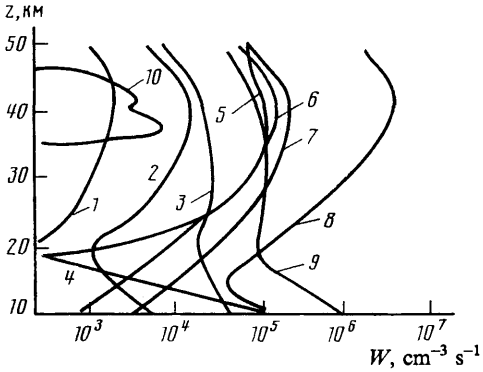


Figure 2. Rates of photochemical formation of radicals of the hydrogen family in the stratosphere:[18] *1*, Cl + H_2; *2*, Cl + H_2CO; *3*, Cl + CH_4; *4*, $CH_3COOH + h\nu \rightarrow CH_3O + OH$; *5*, $H_2O + h\nu \rightarrow H + OH$; *6*, $H_2 + O(^1D)$; *7*, $CH_4 + O(^1D)$; *8*, $H_2O + O(^1D)$; *9*, $H_2CO + h\nu \rightarrow HCO + H$; *10*, generation of OH caused by HNO_3 transport; the rates of processes *5*, *6*, *8*, and *9* are shown on a double scale.

Above 20 km the main source of "odd" hydrogen is provided by the destruction of water vapour

$$O(^1D) + H_2O \rightarrow OH + OH. \quad (23)$$

In the lower stratosphere a similar contribution is made by the photolysis of formaldehyde—one of the intermediates of the oxidation of methane:

$$H_2CO + h\nu \rightarrow HCO + H, (\lambda < 340 \text{ nm}). \quad (24)$$

An alternative channel exists for the photodissociation of formaldehyde

$$H_2CO + h\nu \rightarrow CO + H_2, (\lambda < 340 \text{ nm}) \quad (25)$$

which does not result in the formation of components of the family of "odd" hydrogen. According to Cariolle,[18] the accuracy in determining the quantum yields of these processes is about 40% and for a more rigorous determination of the magnitude of photochemical sources of HO_x in the lower stratosphere careful experimental verification of the relative contribution of each channel in the photodissociation of H_2CO is required.

The photochemical destruction of "odd" hydrogen occurs by a number of processes, resulting in the formation of water molecules:

$$OH+HO_2 \rightarrow H_2O+O_2, \quad (26)$$

$$OH+HNO_3 \rightarrow H_2O+NO_3, \quad (27)$$

$$OH+HO_2NO_2 \rightarrow H_2O+O_2+NO_2. \quad (28)$$

At altitudes of more than 30 km reaction (26) predominates (see Fig. 3). Processes (27) and (28) are predominant at altitudes of 15–30 km. According to one report,[20] the uncertainty factors for the rate constants of these reactions are 1.4 and 2 respectively. Greater accuracy of the kinetic parameters of reactions (23)–(28) is of particular interest currently for processes in the lower stratosphere, where "odd" hydrogen is a key component of the photochemical destruction of ozone.

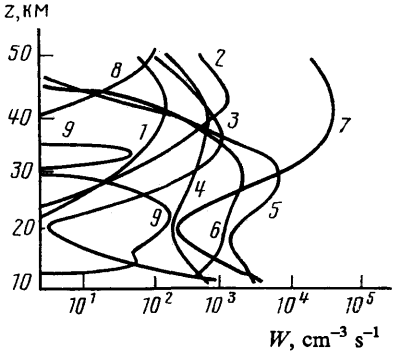


Figure 3. Rates of photochemical destruction of HO_x in the stratosphere[18] (rates of processes *2*, *3*, *5*–*8* are shown on a double scale): *1*, Cl + HO_2; *2*, OH + OH; *3*, OH + H_2O_2; *4*, OH + HCl; *5*, HO_2NO_2 + OH; *6*, OH + HNO_3; *7*, OH + HO_2; *8*, H + HO_2; *9*, depletion of HO_y caused by HNO_3 transport.

The time for equilibrium to be established between the concentrations of OH and HO_2 at stratospheric altitudes does not exceed 10 s (Fig. 1). This is due to the occurrence of a large number of rapid interconversions of OH to HO_2 and the reverse. The vertical profiles of the rates of these reactions are given in Fig. 4.

Despite the comparatively short photochemical lifetimes of the complete family of "odd" hydrogen as a whole and even more so for its individual components (see Fig. 1), dynamic factors can have an averaging effect on the content of HO_y, giving rise to a redistribution of concentrations of the components H_2O and HNO_3 that are important for the balance of HO_y, the lifetimes of which are considerably longer in photochemical reactions.

Virtually all studies in stratospheric photochemistry are in one way or another related to atmospheric ozone—the main component of the oxygen family at these altitudes. The evident progress achieved in this area in recent times does not in any way signify the absence of problems or controversial conclusions, as is reflected by a number of reviews and monographs.[6,7,21–23] We shall only examine certain of those that from our standpoint are of fundamental importance.

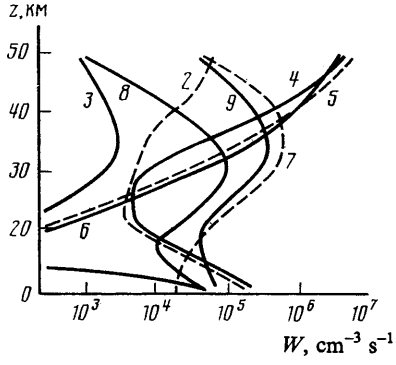


Figure 4. Rates of conversions in the HO_y system (the rates of processes *1* and *3* are shown on a double scale): *1*, $H_2O_2 + h\nu \rightarrow 2OH$; *2*, CO + OH; *3*, $H_2O_2 + h\nu$; *4*, H + O_2 + M; *5*, O + OH; *6*, O + HO_2; *7*, OH + O_3; *8*, HO_2 + O_3; *9*, NO + HO_2.

For several decades the mechanism for the formation and destruction of ozone in the oxygen cycle [reactions (1)–(7)], as proposed by Chapman back in the 1930s, fairly adequately accounted for the results of the majority of full-scale experiments. However, the development of experimental techniques and a refinement of the reaction rate parameters necessitated a review of Chapman's theory, since the stratospheric concentrations of O_3 (particularly in the lower region of the stratosphere) determined by theoretical calculations were considerably higher than the observed concentrations. The possibility that ozone is destroyed in reactions with hydrogen radicals was first demonstrated at the beginning of the 1950s.[8] Subsequently the photochemical destruction of ozone involving nitrogen oxides was examined.[10] A detailed study of the global ozone balance[11] confirmed that in the stratosphere the photochemical generation of ozone substantially exceeds its destruction by the reaction of O + $O_3 \rightarrow 2O_2$, which only accounts for removal of about 20% of the O_3 formed by photolysis of oxygen. The flow of ozone through the tropopause does not exceed 1%. The relative contributions of the nitrogen and hydrogen cycles to the overall photochemical destruction of O_3 (not taking into account the chlorine cycle) from the results of one-dimensional simulation are shown in Table 2. These data are very provisional since similar calculations carried out by different authors suggest that such determinations are sensitive to the rate constants of different reactions and reveal certain quantitative discrepancies. The vertical profiles of the magnitudes of the photochemical destruction of ozone in different cycles are given in Fig. 5.[24] According to current theories the main role in the destruction of ozone in the upper and lower stratosphere is played by the hydrogen cycle while in the middle stratosphere the main role is played by the nitrogen cycle and, to a lesser degree, the hydrogen and chlorine cycles. For the

upper stratosphere the following cycle involving OH and HO_2 is important:

$$\begin{array}{l} OH + O \rightarrow H + O_2, \\ H + O_2 + M \rightarrow HO_2 + M, \\ \hline HO_2 + O \rightarrow OH + O_2, \\ 2O \rightarrow O_2 \end{array} \quad (29)$$

In the mesosphere another series of reactions for the destruction of "odd" oxygen is of greater significance:

$$\begin{array}{l} OH + O \rightarrow H + O_2, \\ H + O_3 \rightarrow OH + O_2, \\ \hline O + O_3 \rightarrow 2O_2. \end{array} \quad (30)$$

In the region of maximum concentration, destruction occurs via the nitrogen cycle:

$$\begin{array}{l} NO + O_3 \rightarrow NO_2 + O_2, \\ NO_2 + O \rightarrow NO + O_2, \\ \hline O + O_3 \rightarrow 2O_2. \end{array} \quad (31)$$

Below 20 km the principle depletion of ozone takes place by a two-step mechanism

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2, \\ HO_2 + O_3 \rightarrow OH + 2O_2, \\ \hline 2O_3 \rightarrow 3O_2. \end{array} \quad (32)$$

However, at these altitudes when certain ratios exist between the background atmospheric concentrations of components of the families of "odd" nitrogen and hydrogen, the radicals can also become involved in competing "zero" cycles:

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2, \\ HO_2 + NO \rightarrow NO_2 + OH, \\ NO_2 + h\nu \rightarrow NO + O, \\ O_2 + O + M \rightarrow O_3 + M, \end{array} \quad (33)$$

or

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2, \\ HO_2 + NO + M \rightarrow HNO_3 + M, \\ HNO_3 + h\nu \rightarrow NO_2 + OH, \\ NO_2 + h\nu \rightarrow NO + O, \\ O_2 + O + M \rightarrow O_3 + M. \end{array} \quad (34)$$

Cycles of this type play the role of a unique buffer, linking the chemically active nitrogen and hydrogen components and reducing the efficiency of ozone destruction.

Moreover, in the lower stratosphere an important photochemical source of ozone is provided by the oxidation of CO, catalysed by nitrogen oxides

$$\begin{array}{l} CO + OH \rightarrow CO_2 + H, \\ H + O_2 + M \rightarrow HO_2 + M, \\ NO + HO_2 \rightarrow OH + NO_2, \\ NO_2 + h\nu \rightarrow NO + O, \\ \hline O + O_2 + M \rightarrow O_3 + M, \\ CO + 2O_2 \rightarrow CO_2 + O_3 \end{array} \quad (35)$$

The source of carbon monoxide in the lower stratosphere (15–20 km) is transport from the troposphere, where CO is mainly formed by oxidation of methane. The strength of this source of ozone (see Table 2) depends mainly on the background concentrations of OH and HO_2 in the lower stratosphere, which remain a subject of controversy even at the present time. That is possibly the reason why in a study of the photochemical balance of the stratosphere[24] carried out using current kinetic data and the results of satellite probing of the global distribution of the most important minor gas components, an imbalance of ozone (an excess of production over destruction in the range 25–60%) was again found at altitudes corresponding to the lower stratosphere. Another source of uncertainty in the determination of the photochemical balance of ozone is the presence of two inconsistent sets of data on the cross-sections of molecular oxygen absorption.[25,26] The use of different data on the cross-sections of O_2 absorption results in a corresponding change in magnitude of the imbalance, as is reflected in Fig. 5. The relative contribution of the different cycles of destruction and formation of ozone can vary considerably as a function of the conditions (altitude, time of day, etc.). For example, the roles of the reactions

$$NO_2 + O \rightarrow NO + O_2,$$

and

$$NO_2 + h\nu \rightarrow NO + O,$$

are quite different. In the first reaction an oxygen atom is consumed while in the second it is formed. Destruction (31) or production (35) of ozone takes place in the nitrogen cycle depending on the ratio of rates of these reactions. Therefore, in the middle stratosphere nitrogen oxides catalyse the destruction of ozone while in the lower stratosphere and in the troposphere the same oxides, being catalysts of the oxidation of CO or hydrocarbons (see Table 2 and below), enable an additional amount of it to be produced.

Table 2. Formation and destruction of ozone in the troposphere (0–14 km) and stratosphere (14–50 km).[39]

Method of calculation	Formation of O_3					Destruction of O_3				
	Process	in the troposphere		in the stratosphere		Process	in the troposphere		in the stratosphere	
		Rate 10^{11} mol cm^{-2} s^{-1}	%	Rate 10^{11} mol cm^{-2} s^{-1}	%		Rate 10^{11} mol cm^{-2} s^{-1}	%	Rate 10^{11} mol cm^{-2} s^{-1}	%
A	Via CH_4	2.9	59.2	0.78	0.3	In the O_x cycle	0.13	0.05	13	5.65
						In the HO_x cycle	3.5	71.4	86	37.4
	Flux from above	2.0	40.8	—	—	In the NO_x cycle	—	—	130	56.5
						Depletion on the earth's surface	1.4	28.6	—	—
B	Via CH_4	33.1	95	12.2	5	In the O_x cycle	—	—	10.1	4,2
						In the HO_x cycle	28.7	83	132	54.5
	Flux from above	1.74	5	—	—	In the NO_x cycle	—	—	100	41.3
						Depletion on the earth's surface	5.9	17	—	—

Note. *A*—when $F_{NO_x} = 10^9$ cm^{-2} s^{-1} and $[CH_4]/[M]$ $(z = 0) = 1.6 \times 10^{-6}$; *B*—when $F_{NO_x} = 10^{10}$ mol cm^{-2} s^{-1} and $[CH_4]/M$ $(z = 0) = 25 \times 10^{-6}$; F_{NO_x} is the flux of nitrogen oxides from the earth's surface, $[CH_4]/[M]$ $(z = 0)$ is the ground level mole fraction of methane.

The depletion of ozone in the chlorine cycle

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2, \\ \underline{O + ClO \rightarrow Cl + O_2,} \\ O + O_3 \rightarrow 2\,O_2 \end{array} \qquad (36)$$

is most significant at high altitudes (30–50 km). The maximum decrease in $[O_3]$ through reactions (36) at the currently accepted levels of freon emissions is estimated at 70% for an altitude of 40 km.[27] In the region of maximum concentration of ozone (20–30 km) the content of ClO and Cl are such ($\sim 10^{-10}$ of [M] at an altitude of 25 km) that the chlorine cycle is not able to compete with the nitrogen cycle (31). Hence, with the flux of freons from the earth currently accepted in calculations, there should be no decrease, rather an increase in $[O_3]$ at altitudes of 15–30 km. The increase in $[O_3]$ is due to the following reaction taking place

$$ClO + NO_2 + M \rightarrow ClONO_2 + M,$$

as a result of which NO_2, the main agent responsible for destruction of ozone, undergoes binding, and hence there is a decrease in photochemical ozone destruction. The increase in concentration of stratospheric ozone due to the flux of freons at altitudes of 15–30 km is 3%. It is thought[27] that at present freons do not cause a significant change in the total content of ozone at middle latitudes, but prognostic calculations indicate the necessity for urgent curtailment of their production.

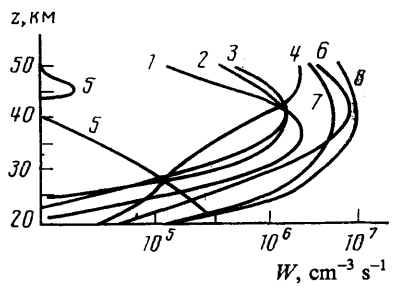


Figure 5. Rates of photochemical destruction and production of ozone in the stratosphere:[24] *1*, nitrogen cycle; *2*, chlorine cycle; *3*, oxygen cycle; *4*, hydrogen cycle; *5*, depletion of ozone through migration; *6*, overall destruction; *7*, overall production at low values of absorption cross-section σ_{O_2}; *8*, the same at higher values of σ_{O_2}.

The decrease in concentration of nitrogen oxides in the middle stratosphere assists an increase in concentration of OH through a reduction in rate of the reaction

$$OH + NO_2 + M \rightarrow HNO_3 + M.$$

On the other hand, an increase in [OH] is inhibited by the reaction

$$OH + HCl \rightarrow H_2O + Cl,$$

in which the primary loss of ClO and Cl is compensated.

Thus, all the families and destruction cycles of ozone prove to be interrelated by a system of complex feedbacks.

An example of the effect of freons is evidently provided by the recently discovered vernal (October–November) "holes" in the ozone layer in Antarctica.[28] The vernal decrease in $[O_3]$ above Antarctica was first noticed in 1979 when it amounted to 10%. From 1959 to 1979 this phenomenon had apparently not yet occurred, while in 1986 the fall in the concentration of ozone was as high as 50%. This recently developed vernal fall in the concentration of Antarctic ozone is most probably due to the effect of ClO radicals.[29–31]

IV. Reactions of OH and HO_2 in the troposphere and oxidation of hydrocarbons. Tropospheric ozone

1. Sources and sinks of "odd" hydrogen in the troposphere

Photochemical sources of HO_x in the troposphere are similar to those in the stratosphere—reaction of water molecules with $O(^1D)$ and the photolysis of formaldehyde, an intermediate in the oxidation of methane. However, under tropospheric conditions, in contrast to those of the stratosphere, it is a considerably more complex task to determine the relative contribution of each of the channels for formation of HO_x in view of the well-known variability of the background concentrations of H_2O and the passage of solar radiation in the region of photodissociation of H_2CO and O_3 and also because of a number of other factors, some of which will be examined below. The mean daily profiles of intensity of the above-mentioned channels under standard atmospheric conditions at 15 and 45 °N are shown in Fig. 6.[32]

The gas-phase photochemical sinks of HO_x in the troposphere are related to reactions in which H_2O molecules are formed:

$$OH + H_2O_2 \rightarrow H_2O + HO_2, \qquad (37)$$

$$OH + CH_3OOH \rightarrow CH_3OO + H_2O, \qquad (38)$$

$$OH + HO_2 \rightarrow H_2O + O_2. \qquad (39)$$

Morover, the presence of water in liquid droplet form in the lower troposphere results in an increased role of heterogeneous processes in the destruction of "odd" hydrogen. This, in particular, denotes that the rainout of a number of reservoir components formed by reactions involving OH and HO_2 in the gas phase

$$OH + NO_2 + M \rightarrow HNO_3 + M, \qquad (40)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (41)$$

constitutes a depletion for the HO_x family in the lower troposphere (Fig. 6).

In the troposphere hydroxyl plays a special role by acting as a unique "cleaning agent". In fact, as follows from Fig. 7, the vast majority of oxidative cycles involving anthropogenic and natural components of gases start with a reaction in which OH participates. At the same time the change in concentrations of hydroxyl and its global distribution have not been studied in sufficient detail in full-scale experiments. This is suggested particularly by the lack of consistency in the results of measurements of the OH content in the troposphere. One of the methods, in which ^{14}CO is used as a tracer for the determination of the average concentrations of tropospheric hydroxyl, yields a value of 1.2×10^6 molecules cm^{-3} for the northern hemisphere.[33] Another, more recent, method is based on measurement of the content of methylchloroform CH_3CCl_3.[34]

This component has an anthropogenic origin that is amenable to global quantitative determination and its sole photochemical tropospheric depletion process is the reaction with OH.

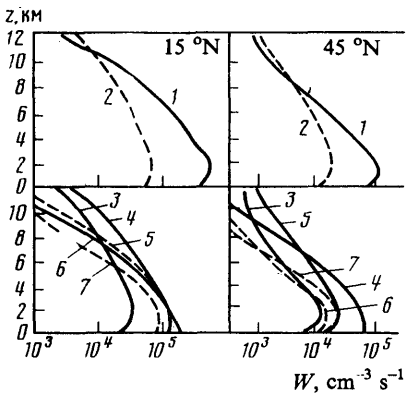


Figure 6. Mean daily rates of photochemical production and destruction of HO_x in the troposphere at 15 and 45 °N:[32] *1*, $O(^1D) + H_2O$; *2*, $H_2CO + h\nu \rightarrow H + HCO$; *3*, $OH + HO_2$; *4*, rainout of H_2O_2; *5*, $OH + H_2O_2$; *6*, $CH_3OH + OH$; *7*, rainout of CH_3OOH.

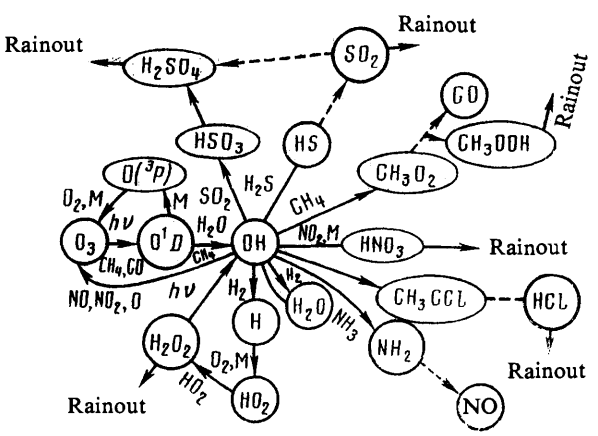


Figure 7. Scheme of photochemical processes involving OH in the troposphere.

Using this method the concentration of hydroxyl is estimated at $3-5 \times 10^5$ molecules cm^{-3} for the northern hemisphere and $0.8-2 \times 10^6$ molecules cm^{-3} for the southern hemisphere.[34] On the whole lower concentrations were generally obtained in model calculations of the global distribution of hydroxyl which were carried out recently compared to the original theoretical predictions.[35] The considerable differences in the content of tropospheric hydroxyl and hydroperoxyl may be due to certain natural factors. Thus, for example, the content of water vapour in the lower troposphere may change over relatively short intervals of time by a factor of 10 or more.[36] Then, since the rate of photolysis of gases in the atmosphere is determined as a convolution of the form

$$j_{A\rightarrow B} = \int_{\Delta\lambda} \sigma_\lambda^A q_\lambda^{A\rightarrow B} F_\lambda d\lambda, \qquad (42)$$

where $\Delta\lambda$ is the spectroscopic range of photodissociation, σ_λ^A is the cross-section of absorption of gas A at wavelength λ, $q_\lambda^{A\rightarrow B}$ is the quantum yield of the reaction, and F_λ is the flux of radiation at that wavelength. The dependence of the average concentrations of OH and HO_2 on incoming solar radiation is evident. The magnitude of F_λ, calculated from the numerical integration of the equation for transmission of solar radiation in the atmosphere, depends on the content of ozone in a column of the atmosphere, molecular and aerosol dispersion, cloud cover, etc.,[32,37] which in turn leads to different concentrations of OH and HO_2. The role of all of the factors listed above is illustrated in Fig. 8, where calculated profiles of the concentration of hydroxyl in the troposphere under different conditions are shown.

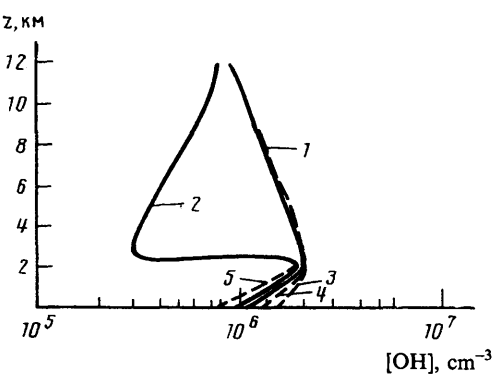
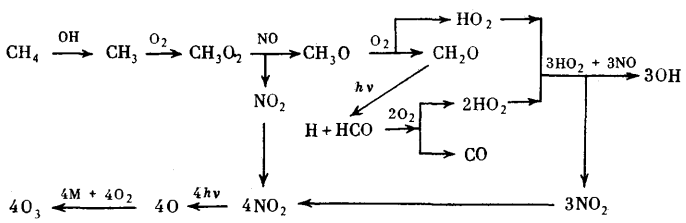


Figure 8. Vertical profiles of the mean daily concentrations of OH for different initial assumptions: *1*, standard atmosphere, contribution of molecular scattering to the photolysis of ozone not taken into account; *2*, profile of H_2O concentration from study of Mastenbrook[36] used for the calculation; *3*, standard atmosphere, contribution of molecular scattering taken into account; *4*, standard atmosphere, molecular scattering and absorption by aerosol taken into account; *5*, standard atmosphere, molecular scattering and absorption by aerosol as well as the effect of globally averaged cloud cover taken into account.

2. Oxidation of methane in the troposphere

The oxidation of CH_4 has a central place amongst the whole set of problems in tropospheric chemistry.[38] It is clear from a simplified scheme of this process that it occurs as a branched chain reaction with degenerate photochemical branching which occurs by photodissociation of formaldehyde. According to scheme (43), three hydroxyl radicals are formed in this case from a single initial one. In reality the branching is of comparatively small importance since a non-radical channel of photodissociation of H_2CO and H_2 and CO exists and because of the high probability of chain termination. It is clear from scheme (43) that on oxidation of a single CH_4 molecule a

maximum of four O_3 molecules can be formed. A further O_3 molecule can be



(43)

formed from carbon monoxide in accordance with reactions (35). In reality less than five ozone molecules are formed by oxidation of a single methane molecule because of destruction of ozone on the earth's surface and in the reactions

$$OH+O_3 \rightarrow HO_2+O_2,$$
$$HO_2+O_3 \rightarrow OH+2O_2,$$

as well as by chain termination in the reactions

$$2HO_2 \rightarrow H_2O_2+O_2,$$
$$HO_2+OH \rightarrow H_2O+O_2,$$
$$OH+NO_2+M \rightarrow HNO_3+M,$$
$$HO_2+NO_2+M \rightarrow HO_2NO_2+M,$$
$$H_2O_2,\ HNO_3,\ HO_2NO_2,\ CH_2O \rightarrow \text{rainout}$$
$$OH,\ HO_2+\text{aerosol} \rightarrow \text{destruction}.$$

The contribution of the oxidation of methane to the production of O_3 in the troposphere was indicated in Table 2. The concentration of the active species OH, HO_2, and O_3 in the troposphere is markedly dependent on the content of methane and on the rate of its oxidation. The latter in turn is a function of the concentration of nitrogen oxides. Nitrogen oxides enter the troposphere directly from the earth and from the stratosphere, where they are formed by the destruction of N_2O. The best agreement between calculations[39] and the results of measuring the average global concentration of tropospheric ozone is achieved when there is a relative concentration of surface methane of 1.6×10^{-6} and a flux of NO_x from the earth of 1×10^{10} molecules $cm^{-2}\ s^{-1}$. The effect of the flux of nitrogen oxides from the earth and the surface concentration of methane on the minor tropospheric components OH, HO_2, O_3, NO_x are illustrated in Figs. 9–11.

The relationship between the photochemical and dynamic factors that affect the shape of the concentration profile of ozone in the troposphere has been the subject of lively debate for more than two decades.[40] At the beginning of the 1960s, when it was established as a result of a series of full-scale measurements that there was a considerable quantity of ozone in the troposphere, its formation there was linked to a flow from the stratosphere through the tropopause (the "transport" theory of tropospheric ozone).[41] At the beginning of the 1980s quite high positive correlations were found between the content of ozone in the troposphere and a number of radioactive products (^7Be) of stratospheric origin,[42] which served as an additional argument in favour of the transport theory. At the end of the 1970s a theory concerning the presence of considerable local photochemical sources of ozone in the troposphere was advanced in parallel.[38] The discovery of the possibility of generating O_3 by oxidising hydrocarbons in the presence of nitrogen oxides was the basis of this. Subsequent measurements and analysis showed, firstly, that there was a close interrelationship between the content of the gas precursors CO and NO_x and the content of ozone in the troposphere and, secondly, that there was an abnormal distribution of O_3 between the northern and southern hemispheres.[43] The latter fact is due, according to current estimates, to a corresponding lack of similarity in global anthropogenic sources of CO and NO_x in the two hemispheres.

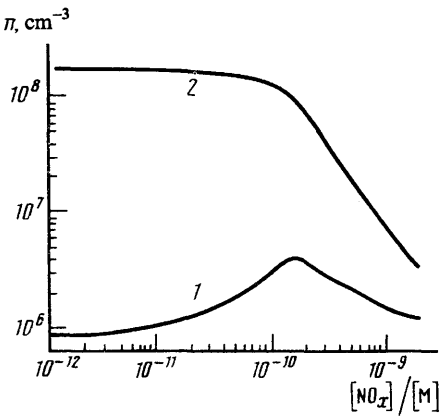


Figure 9. Surface concentrations of OH (*1*) and HO_2 (*2*) as a function of the relative concentration of NO_x, calculated using a one-dimensional model for midday conditions at 45 °N under standard atmospheric conditions ($[CH_4]_{z=0} = 1.6 \times 10^{-6}$).[32]

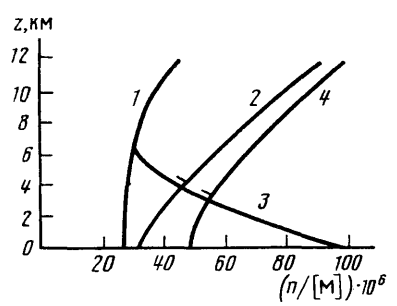


Figure 10. Model concentrations of NO_x (*1* and *3*) and O_3 (*2* and *4*) with different assumptions about the flux of NO_x from the earth's surface[40] and $[CH_4]/[M] = 1.6 \times 10^{-6}$: *1*, *2*, zero flow; *3*, *4*, 2.5×10^{10} molecules $cm^{-2}\ s^{-1}$.

Moreover, there are many feedbacks between the dynamics and photochemistry of tropospheric ozone, which is exhibited particularly in the photochemical destruction of O_3 (including that of stratospheric origin) in the "odd" hydrogen cycle—the main remover of ozone in the troposphere. Furthermore, when there is a high background content of CO, CH_4, and NOx resulting from intense anthropogenic or natural emissions, the role of the photochemical source of ozone increases, the content of O_3 increases

in the troposphere and its flux from the stratosphere to the troposphere decreases because of the levelling out of the vertical gradient of the mole fraction of O_3. The results of numerical simulation, given in Figs. 10 and 11, serve to illustrate the above conclusions. We should note also that all possible types of vertical distribution of ozone concentration in the troposphere observed in full-scale measurements can in principle be simulated by matching the values of the strength of surface sources of the gas precursors of O_3 and the vertical component of the coefficient of turbulent diffusion.[44]

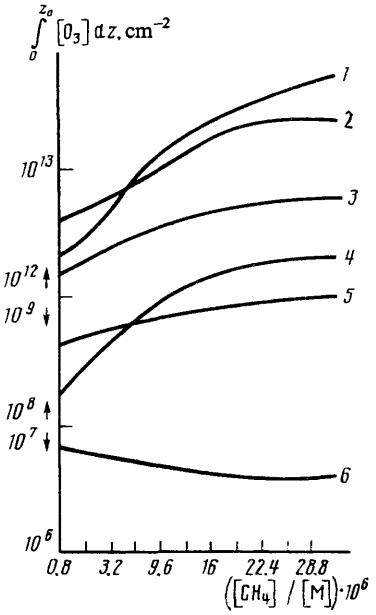


Figure 11. Content of a number of minor gas components in a column of troposphere (0–14 km) as a function of the surface concentrations of methane as determined by one-dimensional simulation.[39] $S_{NO_x} = 10^{10}$ cm^{-2} s^{-1}. *1*, CO × 10^{-5}; *2*, O_3 × 0.5 × 10^{-5}; *3*, NO_2 × 10^{-2}; *4*, CH_3O_2 × 10^{-5}; *5*, HO_2 × 10^{-5}; *6*, OH × 10^{-5}.

The scheme for the oxidation of methane described above can be extended to other members of the hydrocarbon series that are present in the atmosphere of towns and regions with dense anthropogenic sources. Thus, for example, the following sequence of reactions was proposed for ethane:[41]

$$C_2H_6+OH \rightarrow C_2H_5+H_2O,$$
$$C_2H_5+O_2+M \rightarrow C_2H_5O_2+M,$$
$$C_2H_5O_2+NO \rightarrow C_2H_5O+NO_2,$$
$$C_2H_5O+O_2 \rightarrow CH_3CHO+HO_2,$$
$$CH_3CHO+h\nu \rightarrow CH_3+CHO$$

and so on in accordance with the methane oxidation scheme (43). The absence of reliable information about the content of C_2H_6 and the intermediate products of its oxidation in the atmosphere and also the insufficient data on the numerical values of the reaction rate constants makes it difficult to determine the role of C_2H_6, C_3H_8, etc. in the photochemistry of the troposphere.

V. Effect of heterogeneous reactions on the gaseous composition of the troposphere and stratosphere

In addition to a large number of different gases, aerosols also form part of the atmosphere. Aerosols are defined as systems in which particles of a solid and liquid substance are dispersed in a gaseous medium, in this case in the air of the atmosphere.[45,46] The size of aerosol particles can vary from several molecular radii to several tens of microns. It is thought that the main ways of forming aerosols are wind erosion of the soil and the release of particles of salt as a result of the bursting of air bubbles in the break-up of ocean waves. In addition to that, a considerable contribution is provided by anthropogenic sources, the relative proportion of which shows a steady tendency to increase. The difference in the mechanisms of formation and the non-uniformity of the global distribution of sources lead to a considerable variability in chemical composition, size of particles, and concentration of the atmospheric aerosol. In the present review we shall confine ourselves to a very brief examination of the physical and chemical properties of an aerosol in relation to the mechanisms of the possible action of aerosol ensembles on the gaseous composition of different regions of the atmosphere.

1. Tropospheric aerosol

In recent studies of tropospheric aerosol[47–49] it has been customary to subdivide it according to the size of particles into three characteristic bands (modes). The first mode—condensation nuclei—is made up by particles with a radius of less than 0.2 μm, the second mode contains chemically formed and growing particles of radius 0.2–1 μm, and particles with a radius of more than 1μm belong to the third mode—the dispersion mode. The distribution in size of a tropospheric aerosol is usually represented by various approximating relationships using exponential or gamma functions. The vertical profiles of particle concentration can be conveniently defined as exponential functions, the parameters of which are determined from the conditions of the full-scale experiment:

$$N_z = N_0 e^{-z/H_0}, \quad (44)$$

where N_z is the concentration of particles at altitude z, N_0 is their concentration at the surface, H_0 is an experimentally determined parameter. The following model of altitude distribution of an aerosol in the troposphere has been put forward on the basis of statistical treatment of the results of full-scale soundings:[49] the first mode: $N_0 = 10^3-10^5$ cm^{-3}, $H_0 = 2-3$ km; second mode: $N_0 = 5-300$ cm^{-3}, $H_0 = 1.5-2$ km; third mode: $N_0 = 10^{-2}-10^{-4}$ cm^{-3}, $H_0 = 0.5-1$ km. The selection of parameters N_0 and H_0 for specific calculations is determined by the characteristics of the region and the atmospheric conditions (temperature, humidity, etc.).

In the aerosol model of Toon and Pollock[50] the following particle composition in the troposphere was postulated: up to an altitude of 3 km—sulphates 50% [ammonium sulphate $(NH_4)_2SO_4$ is the main form], soil particles (SiO_2, Al_2O_3, Fe_2O_3, etc.) 35%, sea salt (NaCl) 15%; above 3 km—sulphates 60% and soil particles 40%.

According to this model the soil particles have the following elemental composition: SiO_2 53%, Al_2O_3 17%, Fe_2O_3 7%, and other compounds 23%.

2. Stratospheric aerosol

From numerous studies on samples of stratospheric aerosol it can be considered an established fact that its main chemical component under background (undisturbed) conditions is a 75% solution of H_2SO_4. The chemical homogeneity and unimodal distribution of particles by size (usually approximated by the ZOLD function) suggests that a single mechanism for formation of aerosol in the stratosphere predominates It is assumed that this mechanism involves the photochemical conversion of sulphur dioxide and carbonyl sulphide (COS) to sulphuric acid vapour followed by generation of the dispersion fraction as a result of nucleation and condensation. The nature of these processes has so far not been established with sufficient certainty but the most probable channel of SO_2 oxidation is thought to be the following sequence of reactions:

$$SO_2+OH+M\rightarrow HSO_3+M, \quad (45)$$

$$HSO_3+OH\rightarrow H_2O+SO_3 \quad (46)$$

or

$$HSO_3+O_2\rightarrow SO_3+HO_2, \quad (47)$$

$$SO_3+H_2O\rightarrow H_2SO_4. \quad (48)$$

Considerable disturbances of the chemical composition and concentrations of stratospheric aerosol occur after volcanic eruptions. This is due to the injection of a large quantity of sulphur compounds and particles of volcanic ash having a varied elemental composition through the tropopause. Typical profiles of the concentration of aerosol particles under different conditions are shown in Fig. 12.

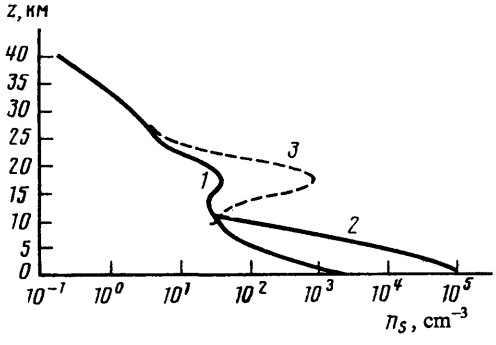


Figure 12. Vertical profiles of the concentration of aerosol particles under different atmospheric conditions: *1*, background (pure) atmosphere; *2*, urban areas; *3*, volcanic clouds.

3. Interaction in the system gases — aerosol. Heterogeneous reactions

Because of the presence of a large number of particles of varied chemical composition in the atmosphere the question as to whether a homogeneous model is applicable for the representation of atmospheric photochemical processes can be raised. In fact, it may be assumed that in a number of situations (urban areas, volcanic aerosol clouds, etc.) heterogeneous destruction on the surface of certain aerosol particles can be an additional form of depletion for chemically active minor gas components. Assuming that under the conditions of a free-molecule system ($Kn = l/\bar{r} \gg 1$) that is characteristic of the stratosphere heterogeneous decomposition occurs as a first-order reaction, the flux of molecules on to a unit surface of aerosol can be given by

$$P = \frac{[n_i]\,\bar{v}}{4} \quad (49)$$

where l is the length of the mean free path, $\bar{r}$ is the average radius of aerosol particles, Kn is the Knudsen number, $\bar{v} = (8RT/\pi\mu)^{1/2}$ is the average arithmetical thermal velocity of the molecules. If γ is the probability of a reaction occurring on collision of a molecule with an aerosol particle, then the number of interactions per unit area per second is

$$Q = \frac{[n_i]\,\bar{v}}{4}\cdot\gamma \quad (50)$$

For a spherical particle the rate of heterogeneous depletion of gas is given by the relationship[51]

$$\frac{d[n_i]}{dt} = -\frac{1}{4}\left\{\frac{8RT}{\pi\mu}\right\}^{1/2}\cdot A\cdot\left(\sum_{j=1}^{k}\gamma_j n_j\right)\cdot[n_i], \quad (51)$$

where $[n_i]$ is the concentration of reacting gas, R is the universal gas constant, T is the temperature, μ is the molecular weight, n_j is the proportion of an aerosol substance of type j relative to the total weight of aerosol, k is the number of possible chemical fractions in the aerosol, $A = 4\pi\bar{r}^2N$ is the specific surface of aerosol particles, $\bar{r}$ is the root-mean-square radius, N is the concentration of aerosol. The last two quantities can be found as the corresponding moments of the given size distribution function of aerosol particles. For small Knudsen numbers ($Kn \lesssim 1$), which is possible in the troposphere, the flow on to a unit of surface can be given by the more general expression:[52]

$$P_1 = \frac{D\,[n_i]}{\bar{r}\,(1+\lambda_0(\gamma))\cdot l/\bar{r}}, \quad (52)$$

where $D = {}^1/_3\bar{v}l$ is the diffusion coefficient, $\lambda_0(\gamma) = \lambda_0(1) + \frac{4(1-\gamma)}{3\gamma}$, with $\lambda_0(1)$ varying monotonically from 1.3 when $Kn \to \infty$ to 0.7 when $Kn = 0$. When $Kn > 1$ and $\gamma \ll 1$ Eqn. (52) transforms to (50). From the relationships obtained it it possible to include heterogeneous processes in equations of the photochemical balance for gas components reacting with the surface of aerosol particles when the corresponding information about their kinetics is available.

4. Model determinations of the possible effect of heterogeneous processes on the gaseous composition of the atmosphere

Before we consider how to represent the results of full-scale studies on the transformation of the gaseous composition of air in the atmosphere in localised zones of aerosol clouds and to a review of laboratory measurements of the rate constants of heterogeneous reactions, let us examine certain boundary measurements obtained with a one-dimensional photochemical model of the atmosphere.[3] The results shown in Figs. 11–13 reflect the degrees of possible variation of the gaseous composition when a model aerosol with given chemical and physical properties is introduced into the

atmosphere. An altitude-invariant profile of the average specific surface of aerosol particles (20 μm^2 cm^{-3}), corresponding to the content of an aerosol in stratospheric volcanic clouds, was used in the calculations.[53] By choosing an altitude-invariant profile it is possible to make a clearer assessment of the sensitivity of different regions of the atmosphere to the introduction of aerosol with given chemical properties. The probability of heterogeneous destruction of the most important minor gas components of the HO_x, O_x, and NO_x families varied over a range of $1-10^{-5}$. The calculations were carried out for a relative surface concentration of methane of 1.6×10^{-6} and a flux of nitrogen oxides $S_{NO_x} = 10^{10}$ molecules cm^{-2} s^{-1}.

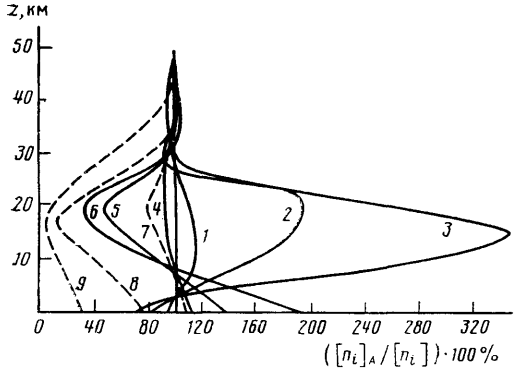


Figure 13. The change in calculated concentrations of certain gases for heterogeneous destruction of O_3 on aerosol particles for different values of y (compared to a purely homogeneous process): *1*, NO_x, $y = 10^{-4}$; *2*, NO_x, $y = 10^{-3}$; *3*, NO_x, $y = 10^{-2}$; *4*, HO_x, $y = 10^{-4}$; *5*, HO_x, $y = 10^{-3}$; *6*, HO_x, $y = 10^{-2}$; *7*, O_3, $y = 10^{-4}$; *8*, O_3, $y = 10^{-3}$; *9*, O_3, $y = 10^{-2}$.

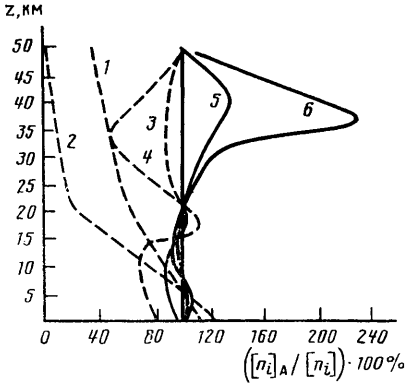


Figure 14. The same as in Fig. 13 but for the case of the destruction of NO_x: *1*, NO_x, $y = 10^{-5}$; *2*, NO_x, $y = 10^{-3}$; *3*, HO_x, $y = 10^{-5}$; *4*, HO_x, $y = 10^{-3}$; *5*, O_3, $y = 10^{-5}$; *6*, O_3, $y = 10^{-3}$.

The changes in concentrations of different gases when an aerosol that destroys O_3 is introduced are shown in Fig. 13. We should note that there is a perceptible deficiency of ozone when $y \geqslant 10^{-4}$, and that heterogeneous destruction of O_3 in the lower stratosphere and upper troposphere (altitude 10–25 km) has the greatest effect on the gas composition. A decrease in the concentration of ozone as a result of its heterogeneous destruction gives rise to a corresponding change in the concentrations of the other components that react with O_3, since the photochemical equilibrium of the system as a whole undergoes an overall shift. It can be established that the calculated deviations in the content of HO_2 and NO_x are generally in good agreement with the main photochemical mechanisms of the stratosphere and troposphere that were examined in the previous sections. Thus, for example, the depletion of ozone in the stratosphere, where the nitrogen cycle is the main cycle of its destruction in the gas phase, results in an increase in concentration of NO_x at these altitudes. In the troposphere, where the destruction of ozone in the hydrogen cycle predominates, the concentration of gases of this family, in particular HO_2, increases.

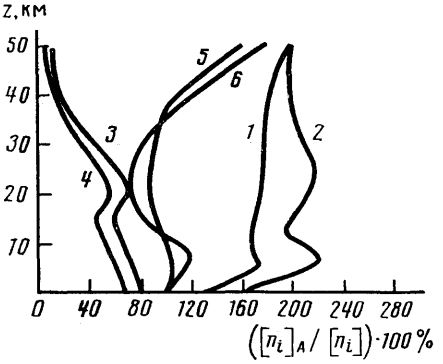


Figure 15. The same as in Fig. 13 but for the case of the destruction of OH: *1*, NO_x, $y = 0.1$; *2*, NO_x, $y = 1$; *3*, OH, $y = 0.1$; *4*, OH, $y = 1$; *5*, O_3, $y = 0.1$; *6*, O_3, $y = 1$.

The second group of model calculations involves a study of the reaction of the system when the heterogeneous destruction of NO_x is introduced (Fig. 14). The critical value of y in this case is about 10^{-5} and the most sensitive region is the upper part of the stratosphere. The nature of the deviations in concentrations of NO_x and HO in Fig. 14 can readily be attributed to the fact that a reduction in $[NO_x]$ causes an increase in O_3 content and increases the consumption of OH and HO_2 in the destruction of ozone. At the same time the content of NO_x increases quite unexpectedly in the lower part of the troposphere despite the development of an additional heterogeneous depletion. This effect may serve as a good illustration of the existence of non-linear feedbacks between the troposphere and stratosphere within the atmospheric photochemical system. In fact the increase in ozone content in the stratosphere as y increases results in a decrease in intensity of the photolysis of ozone via the channel in which $O(^1D)$ is formed in the troposphere because of the screening of UV radiation and hence in a corresponding decrease in the rate of formation of OH by the reaction $H_2O + O(^1D) \rightarrow OH + OH$. This process has the greatest effect on the balance of hydroxyl precisely at altitudes corresponding to the lower troposphere. With a reduced OH content the concentration of NO_x increases, since the effectiveness of its main channel of consumption—$OH + NO_2 + M \rightarrow HNO_3 + M$—is reduced. This

effect more than compensates the heterogeneous destruction of nitrogen oxides in the lower troposphere and becomes more significant when y increases. The calculated data on the change in concentration of the components OH, O_3, NO_x when the heterogeneous destruction of OH is introduced into the model are shown in Fig. 15. A significant change in gaseous composition of the atmosphere is to be expected in this case when $y = 0.1-1$. This change is more apparent in the upper part of the stratosphere, which is quite in accordance with theory. Firstly, the lifetime of HO_x in this region increases in photochemical gas-phase reactions (see Fig. 1), and as a result the relative contribution of heterogeneous depletion to the total destruction of HO_x increases. Secondly, since the hydrogen cycle plays a predominant part in the destruction of ozone in the upper stratosphere, the concentration of O_x increases significantly at altitudes of the order of 40 km when the content of the components at the HO_x family decreases. The introduction of other minor gas components into the balanced equations of heterogeneous depletion has only a slight effect on the calculated concentrations if the aerosol has a specific surface of 20 μm^2 cm^{-3} that is typical of the stratosphere.

Table 3. Probabilities of capture of atmospheric gases by surfaces of different materials.

Gas	Chemical surface	Probability of destruction	Refs.
H_2O_2	H_2SO_4	$7.8\cdot10^{-4}$	[54]
HNO_3	H_2SO_4	$2.4\cdot10^{-4}$	[54]
HO_2NO_2	H_2SO_4	$2.7\cdot10^{-5}$	[54]
N_2O_5	H_2SO_4	$3.8\cdot10^{-5}$	[54]
H_2O	H_2SO_4	$2\cdot10^{-3}$	[54]
NH_3	H_2SO_4	10^{-3}	[54]
OH	H_2SO_4	$5\cdot10^{-4}$	[54]
OH	H_2SO_4	0,1—1	[55]
O_3	Al_2O_3	$(2.3\div8.8)\cdot10^{-5}$	[56]
O_3	H_2SO_4	$\leqslant10^{-8}$	[57]
O_3	H_2SO_4	10^{-10}	[58]
O_3	SiO_2	$\leqslant10^{-4}$	[54]
O_3	Al_2O_3	$5\cdot10^{-5}$	[59]
O_3	SiO_2	10^{-9}	[58]
HO_2	Al_2O_3, Fe_2O_3	$3\cdot10^{-3}$	[60]
OH	SiO_2	$\sim10^{-2}$	[55]
OH	ice	1	[55]

5. Laboratory experiments and stratospheric processes

Examination of models of the chemical composition and the vertical distribution of atmospheric aerosol in combination with the results of numerical simulation indicate that a study of the reactions, of O_3, OH, and NO_x with the surfaces of the most common aerosol particles — H_2SO_4, SiO_2, Al_2O_3, and Fe_2O_3 — is of the greatest interest. In contrast to the rate constants of reactions in the gas phase, comparatively few constants of heterogeneous reactions have been measured, and they have mainly been obtained at room temperature. The existing values, as presented in Table 3, have been obtained during the last 15 years using various experimental techniques. Some of them have been repeatedly verified over this period, since the photochemical balance of ozone is considerably dependent on them. Thus, for example, according to Harker and Ho,[57] the decomposition of O_3 on H_2SO_4 can make a significant contribution to the destruction of stratospheric ozone under background conditions if $\gamma_{O_3} \gtrsim 10^{-4}$. Subsequent experimental measurements[57,58] showed that it does not exceed 10^{-8} even when the surface of sulphuric acid is activated with various metal cations. Thus, even in the presence of volcanic sulphuric acid clouds when the concentration of stratospheric aerosol increases by a factor of 10—100, this process cannot have any substantial effect on ozone depletion. At the same time the results of full-scale probing of the gaseous composition of the stratosphere in localised zones of volcanic aerosol clouds after the powerful eruptions of Agung, St. Helens, and El Chichón suggest that steady negative correlations exist between the concentrations of ozone and aerosol.[61—63] From the value of the probability (0.1—1) of the destruction of OH on the surface of H_2SO_4 obtained using EPR/LMR, Elanskii[63] et al. proposed another mechanism for the deficit of ozone occurring in these situations. It is known from the experimental data that the deficit of ozone in a cloud, reaching a maximum of 30% and with an average value of 7—8%, occurs when the cloud is centred at an altitude of about 20 km. The nitrogen cycle of ozone destruction is characteristic of the photochemistry of the stratosphere in this region, and the conversion of active nitrogen oxides to the buffer components HNO_3 and HO_2NO_2, which are inert towards O_3, mainly involves the members of the family of "odd" hydrogen:

$$OH+NO_2+M\rightarrow HNO_3+M$$

and

$$HO_2+NO_2+M\rightarrow HO_2NO_2+M.$$

It is evident that when there is intense heterogeneous depletion of OH on the volcancic sulphuric acid aerosol, the content of hydroxyl and hydroperoxyl must decrease and the concentrations of nitrogen oxides increase in parallel intensifying the destruction of ozone in the gas-phase photochemical "odd" nitrogen cycle. This mechanism was taken as the basis for a one-dimensional simulation[63] (Fig. 16) using actual aerosol profiles obtained in probes of volcanic clouds after an eruption of the El Chichón volcano.[53] Another probable mechanism for the destruction of O_3 involves its decomposition on an aerosol containing Al_2O_3. However, although the aerosol particles containing Al_2O_3 can pass into the stratosphere together with volcanic ash during powerful eruptions, they are not likely to have a significant effect on ozone because of rapid precipitation. The emission of this type of aerosol into the stratosphere in quantities that are capable of giving rise to a competing gas-phase depletion are only possible with intense artificial effects, in particular, from nuclear explosions on the earth's surface. This situation has been analysed in detail by Zvenigorodskii et al.[3]

In summing up let us make two observations of a general nature.

1) Despite the fact that the decomposition constants of O_3 on Al_2O_3 obtained by different authors are in good agreement, the question of the degree of correspondence between the properties of a laboratory sample (pellets of pure Al_2O_3) and those of a real aerosol, in which Al_2O_3 is in the form of conglomerates and undergoes natural ageing and the effect of water vapour, remains open.

2) It is unlikely that the catalytic properties of a stratospheric sulphuric acid aerosol differ very much from the properties of the surface of H_2SO_4 in laboratory experiments. Therefore, the experimentally determined rate constants of the reactions of different gases with H_2SO_4 can be reliably used in solving problems of

atmospheric chemistry. Nevertheless, there is no significant information about the catalytic activity of H_2SO_4 towards nitrogen oxides.

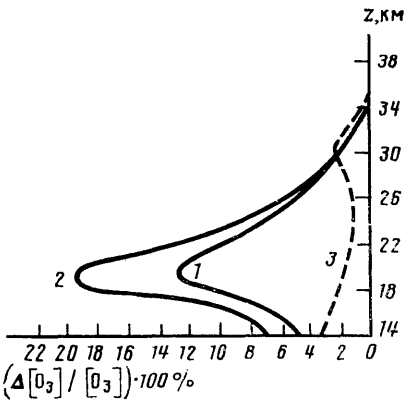


Figure 16. Decrease in the concentrations of ozone in the stratosphere in relation to the capacity and altitude of the maximum of a volcanic aerosol cloud:[63] *1*, maximum at an altitude of 20 km, A_{max} = 20 μm² cm⁻³; *2*, the same, A_{max} = 50 μm² cm⁻³; *3*, maximum at an altitude of 30 km, A_{max} = 20 μm² cm⁻³.

6. Heterogeneous processes in the troposphere

The aerosol fraction in the troposphere varies according to its chemical composition and aggregate state—droplets of moisture and ice crystals, irrigated and unirrigated aerosol particles. If the well-defined variability in the composition of a tropospheric aerosol is also taken into account, this all considerably hinders determinations of the effect of heterogeneous factors on photochemical processes in this region. Moreover, the active lower boundary—the underlying surface—is a sink on a global scale for a whole number of gas components. Originally, in studying heterogeneous processes in the troposphere research workers confined themselves to two mechanisms: rainout of gases that are soluble in water by precipitation (wet rainout) and the destruction of gas-phase components on the underlying surface (dry deposition). The dry deposition of gases occurs through their adsorption or destruction in chemical reactions on the surface. The evident consequence of a chemically active lower boundary is the presence of a concentration gradient and diffusive flow of molecules directed towards the surface that react with the earth, which in atmospheric chemistry can be identified with the "deposition" of a complete column of reacting gas. The rates of dry deposition of a number of gases have been measured under artificial conditions[64–66] above different underlying surfaces. This process can have a definite effect on the content of chemically active gases in the lower part of the troposphere, for example, in seasonal changes in the nature of the surface (Fig. 17).[67]

Wet rainout in the troposphere was for a long time reduced to the removal of precipitation of soluble gases and those reacting in water. A typical time for this process according to initial estimates corresponds to the time of global cycle of tropospheric moisture and amounts to about 10 days. It is evident that such a scheme for representing heterogeneous processes in the troposphere, also accepted in a number of current photochemical models designed for studying mechanisms of the global distribution of gas components, is a considerable simplification of the real picture.

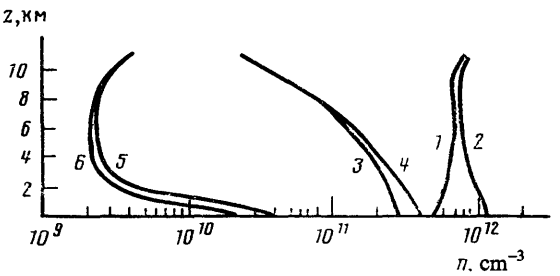


Figure 17. Vertical profiles, of O_3, NO_x, and HO_2 concentrations in the troposphere for different rates of ozone deposition on the surface:[67] *1*, concentration of O_3 for a rate of deposition W_{O_3} = 0.6 cm s⁻¹ (earth); *2*, the same for W_{O_3} = 0.02 cm s⁻¹ (snow); *3*, $[HO_x] \times 10^3$, W_{O_3} = 0.06 cm s⁻¹ (earth); *4*, $[HO_x] \times 10^3$, W_{O_3} = 0.02 cm s⁻¹ (snow); *5*, $[NO_x] \times 10$, W_{O_3} = 0.6 cm s⁻¹ (earth); *6*, $[NO_x] \times 10$, W_{O_3} = 0.02 cm s⁻¹ (snow).

Firstly, atmospheric gases have varying solubility, as determined by Henry's constant.

Secondly, the partial return to the atmosphere of gases that are not dissociated in water on evaporation of water droplets is not taken into account.

Thirdly, an important role is played in the troposphere by heterogeneous processes involving an irrigated and unirrigated aerosol.

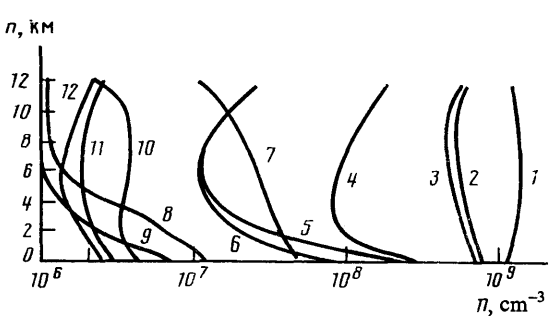


Figure 18. Calculated concentrations of HNO_3 (*1–4*), NO_x (*5–8*), and HO_x (*9–12*) for rate constants of rainout K_z, s⁻¹ of: 0 (*1, 5, 9*); 1.15 × 10⁻⁶ (*2, 6, 10*); 5 × 10⁻⁶ (*3, 7, 11*); 10⁻⁵ (*4, 8, 12*).[67]

It is clear that a description of heterogeneous chemical processes in the troposphere must be based on a consideration of all types of reactions taking into account the individual properties of a reacting

gas. Up to the present time the complete absence of experimental data on the probabilities of capture of molecules which interact with an aqueous surface remains the main problem. The calculation of the integrated rate of washout of gases in atmospheric cloud and aerosol systems based on the solution of kinetic equations for a single particle followed by generalising it for an ensemble of particles with a given size distribution function does not present major difficulties, but in all the overall relationships thus obtained the probability of capture appears as a parameter.[68] The only current method for independent determination of the rates of rainout is based on measurement of the chemical composition of the deposits. However, in this case other sources of uncertainty arise, related to assumptions about the exposure time of the droplet, the chemistry of liquid-phase processes, and errors in the measurements themselves, which considerably reduce the accuracy of the estimates obtained.

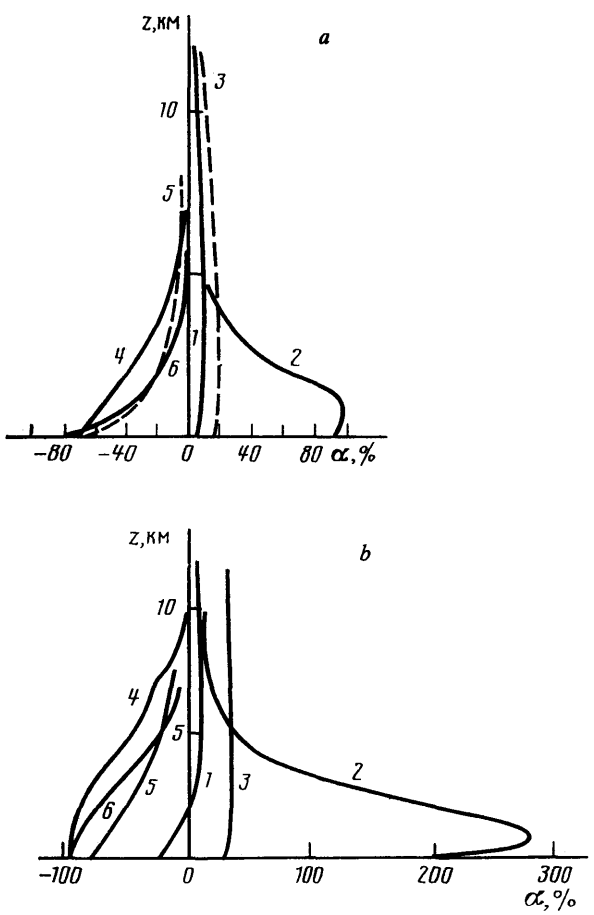


Figure 19. Change in the relative concentrations of O_3 (*1*), NO_2 (*2*), CO (*3*), H_2O_2 (*4*), OH (*5*), and HO_2 (*6*) when the destruction of OH (*a*) and HO_2 (*b*) radicals on aerosols is taken into account: *a*, $\gamma_{OH} = 1$; $N = 5 \times 10^4 \exp(-z)$ cm^{-3}; *b*, $\gamma_{HO_2} = 8 \times 10^{-3}$; $N = 5 \times 10^5 \exp(-z)$ cm^3.

Because of these factors, it would seem natural to assume that the washout constants in the existing photochemical models of the troposphere must differ considerably. And in fact, a scatter of the order of magnitude of 10^{-5} to 10^{-6} s^{-1} is reached. Thus, Logan[32] recommended that for the simulation of wet rainout of H_2O_2, HNO_2, HNO_3, HO_2NO_2, H_2CO, and CH_3OOH the following values of the constants should be used: up to an altitude of $z = 4$ km, $k = 2.31 \times 10^{-6} \exp(1.6-0.4z)$ s^{-1}; and when $z > 4$ km, $k = 2.31 \times 10^{-6}$ s^{-1}. The rate constant of the additional depletion of H_2O_2 on an irrigated aerosol in the continental troposphere was given by the expression: $2 \times 10^{-6} \exp(-z/1.2) + 4 \times 10^{-8}$ s^{-1}. The latter relationship was obtained with the assumption that the whole aerosol is irrigated, H_2O_2 is irreversibly destroyed in the aqueous shell of aerosol particles by interacting with the ferrous cation Fe^{2+} and the probability of capture is the same as for the surface of sulphuric acid,[54] namely 10^{-3}. It has already been mentioned that a general deficiency of current photochemical models of the troposphere that represent rainout of gases by precipitation is the use of the same relationships for a whole series of components that are susceptible to rainout for a determination of the parameters of this process, without taking into account their individual properties. At the same time even the few results of analysis of the chemical composition of deposits show that in the hydrocarbon series, for example, H_2CO is rained out to a much lesser extent than other members of the series, since the concentrations of formaldehyde in the analysed samples of rainwater are low.[69,70] Moreover, as is demonstrated by model calculations, the concentrations of the minor gases in the lower part of the troposphere are very dependent on the rainout rate constants. Numerical experiments to determine the concentrations of minor gases when the rate constants of rainout vary over the wide range of $0-10^{-5}$ s^{-1} (Fig. 18) show that in this case these concentrations vary over several hundred percent.[67]

In recent times because of the problem of acid rain, composite photochemical models of the troposphere that combine theories about the chemical processes in the vapour and liquid phases have started to be developed.[70,71] However, a weak point of these models is still the same lack of data on the coefficients of capture.

Heterogeneous reactions on the surface of an unirrigated aerosol should also be made the subject of careful study. As was indicated earlier, attempts to examine the interaction between an aerosol and gases in the atmosphere that are based on the assumption that the whole aerosol is irrigated frequently yield results that do not correspond to current ideas about the physicochemical processes in this region. The clearest example is provided by the study of Isaksen and Crutzen,[72] in which a similar approach using the assumption of an aerosol sink results in the deviations of the calculated concentrations of H_2O_2 and HO_2 from those observed reaching two orders of magnitudes. The incorrectness of such an approach is suggested also by the results of many experiments on irrigation of aerosols in clouds and mists. Thus, for example, it was found that 100% irrigation only occurs for large submicron particles, whereas out of the total number of particles with a radius of < 0.4 μm, in which about 90% of the total surface of a stratospheric aerosol is concentrated, not more than 2% is irrigated.[46] Thus, it is evident that the role which an unirrigated tropospheric aerosol plays in heterogeneous chemical processes in the troposphere is at least comparable to the role of irrigated and droplet aerosols. Gershenzon et al.[4] studied the change in gaseous composition of the troposphere taking into account the possibility of heterogeneous destruction of OH and HO_2 radicals on the surface of model aerosols. From the results of two studies[55,60] typical values for a tropospheric aerosol are $\gamma_{OH} = 0.1-1$ and $\gamma_{HO_2} = 10^{-3}-10^{-2}$. The results of a calculation[4] of the values of $\alpha = [(n_A - n)/n] \times 100$

(n_A and n are the concentrations of the minor components in aerosol and molecular atmospheres respectively) are presented in Fig. 19. The calculations were carried out for aerosols with an average radius of 10^{-5} for an altitude distribution of their concentration in accordance with the equation $N = N_0 \exp(-z)$. The results suggest that there is a decrease in concentrations of the active compounds of the hydrogen family (OH, HO_2, H_2O_2) and an increase in content of CO, O_3, and NO_x in the aerosol troposphere as a result of the heterogeneous destruction of OH and HO_2.

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Expert evaluation of kinetic data for use in research on atmospheric modelling

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ABSTRACT. The development of data banks on chemical kinetics and photochemistry for use in modelling the atmosphere is examined. A table representing a compilation of data on the chemistry of the formation of stratospheric ozone in which the reactions are grouped into families (O_x, HO_x, NO_x, ClO_x, and organic reactions) is published. An approach to the selection of the recommended values of kinetic and photochemical quantities, developed by CODATA/IUPAC experts, is described in detail. The review is completed by a brief discussion of the immediate prospects for the development of expert evaluations of data for atmospheric chemistry.

The bibliography includes 40 references.

Contents

I.	Introduction	945
II.	Families of reactions in atmospheric chemistry	946
III.	Format for the presentation of data	947
IV.	Compilation of lists of data	947
V.	Table of reactions and recommended kinetic quantities	957

I. Introduction

Studies on expert evaluations of kinetic data for use in atmospheric modelling were initiated in 1971 by the Information Centre on Chemical Kinetics at the National Bureau of Standards (Washington). They were stimulated by the suggestion that, as a consequence of chemical reactions involving nitric oxide ejected by supersonic aeroplanes, a significant decrease in the ozone content of the stratosphere might take place[1,2]. Studies on expert evaluations of kinetic data at the National Bureau of Standards soon included in the Program for the Evaluation of Influences on the Climate (Department of Transportation of the USA). This program was started in 1970–1971 with the aim of determining the possible ecological consequences of the pollution of the stratosphere by aeroplane exhausts. A characteristic feature of the program involved studies designed to estimate the photochemical and kinetic parameters of stratospheric reactions: these investigations were published in the open press and also in the reports of the National Bureau of Standards[3,4].

In September 1975 the CODATA Expert Panel on Chemical Kinetics held an international symposium on "Kinetic Data for the Upper and Lower Atmosphere". This symposium and its published proceedings[5] constituted the cornerstone in establishing the importance of kinetic information for the chemistry of the atmosphere.

In 1976 the National Aeronautics and Space Administration of the USA (NASA) assumed the duty of assessing the influence of the released **u**reons on stratospheric ozone. The next landmark in the creation of surveys of data on atmospheric processes was the NASA publication 1010 "Chlorofluoromethanes and the Stratosphere"[6]. This publication became the first of the regular surveys of kinetic and photochemical data for stratospheric modelling which are prepared by the NASA Expert Panel, and is published by the Jet Propulsion Laboratory in Pasadena (California). Approximately one review has been published every 18 months in this series since 1977. Communication No. 9 has already been published and work of this kind is being continued.

Together with the start of the NASA publications, the necessity for organising an international Expert Panel for the preparation of surveys of kinetic parameters for reactions relevant to atmospheric chemistry was recognised. The principal feature of this approach was the global nature of the object of study. The CODATA Working Group on Chemical Kinetics has been newly created under the aegis of the International Council of Scientific Societies. The first publication of this international group[8] dates back to 1980. Supplements were issued in 1982, 1984, and 1989.[9] The last of these communications was prepared by the IUPAC Subcommittee for the evaluation of data for atmospheric chemistry which has replaced the CODATA Working Group and has continued to work on surveys of kinetic data.

The NASA Expert Panel and the CODATA/IUPAC Group have collaborated closely during the last 13 years. The NASA surveys are published more frequently and are aimed at stratospheric chemistry whereas the CODATA/IUPAC surveys include both stratospheric and tropospheric reactions. Both groups have prepared a general survey of data for inclusion in the report by the World Meteorological Organisation "the Stratosphere" [10].

The creation of these two independent Expert Panels, supplementing one another, has made it possible to solve the difficult problem of evaluating kinetic and photochemical data on a collective basis. The NASA Panel (USA) has at its disposal the national system for the dissemination of data whereas the IUPAC International Subcommittee has a broader base but publishes its surveys more rarely.

This communication considers the approach used and the results of the surveys of the IUPAC Subcommittee on Kinetic and Photochemical Data for Atmospheric Chemistry.

As an illustration, a list of data for one of the reactions is given and there is also a complete list of reactions together with the recommended rate constants and errors

II. Families of reactions in atmospheric chemistry

In 1930 Chapman put forward a photochemical theory of the formation of stratospheric ozone in reactions involving species containing oxygen alone[11,12]:

$$O_2 + h\nu \rightarrow O + O, \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M, \quad (2)$$

$$O_3 + h\nu \rightarrow O + O_2, \quad (3)$$

$$O + O_3 \rightarrow 2O_2. \quad (4)$$

These reactions constitute the basis of the O_x family. Reactions of vibrationally and electronically excited species were recently added to this family (see Section V).

The measurements of the rate constants for reaction (4) carried out in the 1950s showed that the reaction is much slower than had been believed at the time when Chapman proposed his theory. The concentration of ozone calculated on the basis of reactions (1)–(4) by the method of stationary concentrations proved to be higher than that observed in the atmosphere. In order to account for this discrepancy, Hunt[13] suggested that the HO_x species (H, HO, HO_2), first introduced by Bates and Nicolet[14], participate in the ozone destruction catalytic cycles:

$$H + O_3 \rightarrow HO + O_2, \quad (5)$$

$$\frac{HO + O \rightarrow H + O_2,}{\text{total } O + O_3 = 2O_2.} \quad (6)$$

$$HO + O_3 \rightarrow HO_2 + O_2, \quad (7)$$

$$\frac{HO_2 + O \rightarrow HO + O_2,}{O + O_3 = 2O_2.} \quad (8)$$

$$HO_2 + O_3 \rightarrow HO + 2O_2, \quad (9)$$

$$\frac{HO + O_3 \rightarrow HO_2 + O_2,}{O_3 + O_3 = 3O_2.} \quad (10)$$

Reactions (5)–(10) form part of the family of the HO_x reactions presented below in Table 2.

The next step in the development of the theory of the photochemical formation of ozone occurred at the beginning of the 1970s when Crutzen[1] proposed a catalytic cycle with participation of NO_x. Johnston[2] suggested soon afterwards that the nitrogen oxides from the exhausts of supersonic aeroplanes lead to the depletion of the ozone layer, which has serious consequences as a result of the increase in the transparency of the atmosphere to ultraviolet rays.

$$NO + O_3 \rightarrow NO_2 + O_2, \quad (11)$$

$$\frac{NO_2 + O \rightarrow NO + O_2,}{O + O_3 = 2O_2.} \quad (12)$$

The family of the NO_x reactions, presented below in Table 2, was thus introduced into consideration. It shows that there is an appreciable interaction between the catalytic NO_x cycle, the HO_x and ClO_x families (see below). One of the pathways in such interaction involves reactions which have a direct influence on the conversion of the NO_x and ClO_x species into other active forms, for example:

$$HO_2 + NO \rightarrow HO + NO_2, \quad (13)$$

$$ClO + NO \rightarrow Cl + NO_2. \quad (14)$$

The hypothesis by Molina and Rowland[15] that the chlorine atoms formed on photochemical decomposition of chlorofluorocarbons (CFC) in the upper atmosphere can lead to an appreciable destruction of ozone in the catalytic cycle

$$Cl + O_3 \rightarrow ClO + O_2, \quad (15)$$

$$\frac{ClO + O \rightarrow Cl + O_2,}{O + O_3 = 2O_2.} \quad (16)$$

made the problem of the decomposition of the ozone layer still more acute. Subsequently an appreciable number of supplementary reactions were added to the ClO_x family (see Table 2 below).

Chlorofluorocarbons accumulate rapidly in the atmosphere and, because of their long lifetime, it would be impossible to neutralise their influence in the foreseeable future. A need therefore arises for predictive mathematical models capable of describing the behaviour of atmospheric ozone now and in the future. Such models have been vigorously developed during the past 15 years. One-dimensional models with transport are being replaced nowadays by two-dimensional (width–height) models. Both types of models include 150 elementary gas phase chemical and photochemical reactions. The characteristics of these models as well as kinetic data banks have been periodically considered in reviews, so that the prediction of the changes in the ozone content rests on a reliable scientific basis.

The report[16] of a significant decrease in the amount of ozone during springtime over the Antarctic ("ozone hole") in 1985 was very unexpected. Models did not predict such changes. The subsequent vigorous field and laboratory studies revealed new chemical processes in the lower stratosphere. These include heterogeneous reactions on the surfaces of polar stratospheric clouds which are formed on condensation of water vapour with an admixture of nitric acid. These reactions convert a large proportion of chlorine into a catalytically active form. Thus it was shown that chlorine constitutes a serious threat to ozone. These studies led to attempts to replace the long-lived chlorofluorocarbons by substances with similar properties but more readily removed from the atmosphere, for example, by reaction with the HO radicals in the troposphere.

Tropospheric chemistry has become a rapidly developing field after it was suggested that there are high stationary concentrations of HO and HO_2 in the troposphere in the presence of sunlight.[17] Since HO radicals are highly reactive, the reactions with them constitute an important sink for the majority of trace impurities. Further progress in tropospheric chemistry is associated with the study of the photochemical formation of oxidants or smog. Demerjian et al.[18] were the first to formulate the mechanisms of the oxidation of hydrocarbons in the presence of NO_x with formation of ozone in polluted air. Kinetic data for the modelling of tropospheric chemistry are presented in Table 2 in the "Organic reactions" Section.

The complexity of both tropospheric and stratospheric chemistry requires accurate data for a multiplicity of elementary gas-phase reactions. Expert evaluation of data has played a major role in combining experimental and theoretical information. In the sections which follow in this review, an approach is described to the evaluation of data for atmospheric chemistry.

III. Format for the presentation of data

At the beginning of studies concerning the expert evaluation of chemical and photochemical data, the CODATA Working Group had to select a suitable format for the presentation of data. Previous reviews were either detailed, involving a detailed consideration of individual measurements, for example, the reviews on high-temperature kinetics[19], or were abbreviated, as in the early Tables of the National Bureau of Standards[4]. The CODATA Group selected an intermediate degree of detail: the experimental methods and conditions are indicated and the discrepancies between the results of different studies are discussed. This was achieved by employing the "list of data" approach in which information is compiled and discussed in a standardised form for each elementary reaction. The reactions were grouped in terms of the O_x, HO_x, NO_x, organic, SO_x, FO_x, ClO_x, BrO_x, and IO_x families.

IV. Compilation of lists of data

1. Thermal reactions

The list of data[19] is begun with the formation of the reaction equation taking into account all of its feasible pathways. Next, the enthalpy change at 298 K is quoted. The available kinetic data are presented in four sections—the rate constants obtained from absolute and relative measurements, branching parameters, and recommended constants with an indication of the Expert Panel.

Since all the reactions considered are elementary chemical processes, the expression for the rate of reaction is formulated in accordance with the reaction equation:

$$A + A \rightarrow B + C,$$
$$-1/2\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2.$$

Thus the stoichiometric coefficient 2 for A appears in the denominator before the rate of change of [A] {it is equal to $2k[A^2]$} and in the power exponent in the right-hand side of the equation.

The rate constants for reactions are presented in the form of the simple Arrhenius equation: $k = A\exp(-B/T)$, where $B = E/R$ can be both positive and negative. For the pressure-dependent recombination and dissociation rate constants, a non-Arrhenius temperature variation is used, which is discussed in the next Section.

The kinetic data are provided with commentaries in which experimental details are described. The recommended rate constants are quoted for 298 K and also in the form of a temperature variation equation for the temperature range indicated. The errors in $\lg k$ at 298 K and in the values of E/R in the temperature range of the recommended rate constants are indicated. The choice of the recommended values is justified in the commentary and other relevant information is presented.

A typical list of data for the thermal reaction $HO + HCHO \rightarrow H_2O + HCO$ is presented in Table 1.

2. Recombination and dissociation reactions

The rates of recombination and dissociation reactions depend on the temperature T, the nature of the species, and the concentration of the third body M:

$$A + B + M \rightarrow AB + M.$$

Table 1. Typical list of data from a CODATA survey[9]

$HO + HCHO \rightarrow H_2O + HCO$, (1)
$HO + HCHO \rightarrow H + HCOOH$, (2)
$\Delta H°(1) = -135.3$ kJ mol^{-1},
$\Delta H°(2) = -91.5$ kJ mol^{-1}
The rate constant $k = k_1 + k_2$.

k, cm^3 s^{-1}	T, K	Refs.	Remarks**
Absolute measurement			
$(8.1\pm0.5)\cdot10^{-12}$	296	[20]	1
$(1.66\pm0.20)\cdot10^{-11}\exp(-86/T)$	296—576	[21]	2
$(1.25\pm0.11)\cdot10^{-11}$	298		
Relative measurements			
$(8.4\pm0.5)\cdot10^{-12}$	299	[22]	3
Branching parameters			
$k_1/k = 1.00\pm0.05$	296	[20]	1
$k_2/k < 0.02$	299	[22]	3
Values recommended previously			
$1.1\cdot10^{-11}$	200—425	[23]	4
$5.0\cdot10^{-11}\exp(-600/T)$	300—2500	[24]	5
$1.0\cdot10^{-11}$	228—426	[25]	6
$9.0\cdot10^{-12}$	228—426	[26]	7
$5.7\cdot10^{-15}T\,1.18\exp(225/T)$	300—1660	[27]	8
$1.0\cdot10^{-11}$	228—426	[28]	6
Recommended values*			
$1.1\cdot10^{-11}$	298	—	—
$1.6\cdot10^{-11}\exp(-110/T)$	230—580	—	—
$k_1/k = 1.0$	298	—	—

Reliability
$\Delta\lg k = \pm0.1$ at 298 K
Determination of errors
$\Delta(E/R) = \pm150$ K;
$\Delta(k_1/k) = \pm0.1$ at 298 K

* The recommended values were obtained by the method of least squares using the absolute rate constants determined in a number of investigations[20,21,30,31] and agreeing well with one another at room temperature. The results of relative measurements obtained in several investigations[22,29,34] correspond to the recommended values at 298 K. Analysis of the products[20,22] showed that at 298 K this reaction proceeds predominantly via pathway 1 with formation of H_2O + HCO.

** The figures in the remarks column have the following significance; (1) discharge flow—detection of HO and HCO radicals by the laser magnetic resonance method. The ratio k_1/k was obtained by comparing the amount of HCO formed with the amount of HO which had reacted; (2) laser photolysis—detection of HO by the laser-induced fluorescence method; (3) method of relative rates. The HO radicals were generated by the photolysis of $CH_3ONO-NO-$air and $C_2H_5ONO-NO-$air mixtures at an overall air pressure of 700 mmHg. The rates of disappearance of $H^{13}CHO$ and C_2H_4 were determined by IR spectroscopy. The rate constant ratio $k/k(HO + C_2H_4) = 0.99 \pm 0.06$ was converted into the absolute value assuming that $k(HO + C_2H_4) = 8.5 \times 10^{-12}$ cm^3 s^{-1} [26]. The ^{13}C isotope effect was neglected. The ratio $k_2/k = 0.02$ was estimated on the basis of the absence of $H^{13}COOH$ from the products; (4) obtained as the average of the rate constants determined in a number of studies[29—31]; (5) based mainly on rate constant data[30,32,33]; (6) the rate constant at 298 K is the mean of the absolute values determined in two studies[30,31]. These data do not indicate any temperature dependence of the rate constants; (7) obtained from values determined in a number of investigations[20,22,30,31] on the assumption that the rate constant is independent of temperature[24,30]; (8) based on a number of data[30—33].

The rate constants for such reactions should be expressed in a more complex form than the rate constants for simple bimolecular reactions. Recombination reactions are described in terms of a pseudo-second order law:

$$\frac{d[AB]}{dt} = k[A][B].$$

Here the second-order rate constant k depends on [M]. The low pressure limit for the third-order rate constant is characterised by a quantity k_0 proportional to [M]:

$$k_0 = \lim_{[M]\to 0} k([M]).$$

The high pressure limit (the bimolecular constant) is characterised by a quantity k_∞ which is independent of [M]:

$$k_\infty = \lim_{[M]\to \infty} k([M]).$$

For recombination reactions in the region of low pressures, Table 1 presents second-order rate constants expressed as the product of the third-order rate constant and the concentration of the third species. The transition between third- and second-order regions is described by the equation quoted for the decrease in k/k_∞ as a function of

$$k_0/k_\infty = [M]/[M]_c,$$

where the "centre of the decrease curve" $[M]_c$ denotes the concentration of the third species at which the extrapolated value of k_0 coincides with k_∞. This is illustrated in uig. 1. The dependence of k on [M] is generally speaking complex and the theory of unimolecular reactions has to be applied in its analysis. However, for moderately complex molecules in the region of not unduly high temperatures, an approximate expression is applicable:

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \frac{1}{1 + [M]/[M]_c} F = k_\infty \frac{[M]/[M]_c}{1 + [M]/[M]_c} F,$$

where the first terms represent the Lindeman–Hinshelwood equation and the additional expanding multiplier F at not unduly high temperatures is specified[35–37] by

$$\lg F \simeq \frac{\lg F_c}{1 + [\lg([M]/[M]_c)]^2}.$$

Thus, three quantities—k_0, k_∞, and F_c together with

$$[M]_c = \frac{k_\infty}{k_0/[M]}$$

characterise the decrease curves for the purpose under consideration. It is also possible to employ the quantities k_∞, $[M]_c$, and F_c or k_0, $[M]_c$, and F_c. The temperature variation of F_c, which is significant in certain cases, can be estimated by Troe's method[35–37]. The results are usually represented by the approximate equation

$$F_c = (1-a)\exp(-T/T^{***}) + a\exp(-T/T^{*}) + \exp(-T^{**}/T).$$

The first two terms are significant under atmospheric conditions, while the third term begins to contribute in most cases at much higher temperatures. In the first reviews, it was assumed for simplicity that $a = 1$ and that $T_c^{**} \simeq 4T^{*}$. If the values of F_c are known for only one temperature, then the approach remains the same. The term $\exp(-T^{**}/T)$ is frequently negligible at temperatures below 300 K. However, for a more detailed consideration, it is necessary to determine a, T^{***}, T^{*}, and T^{**}. Theoretical predictions[35–37] have been made with the aid of rigorous models of the RRKM type taking into account the influence of weak collisions. For reactions which are significant in the atmosphere, systematic calculations of this type have been published by Patrick and Golden[38]. The question whether these calculations are applicable to barrier-free radical recombination reactions, where rotation effects are important, remains open. The changes in F_c may require changes in the limiting quantities k_0 and k_∞. For the purposes of the present review, this is insignificant in most cases if the recommended values of k_0 and k_∞ agree with the recommended F_c.

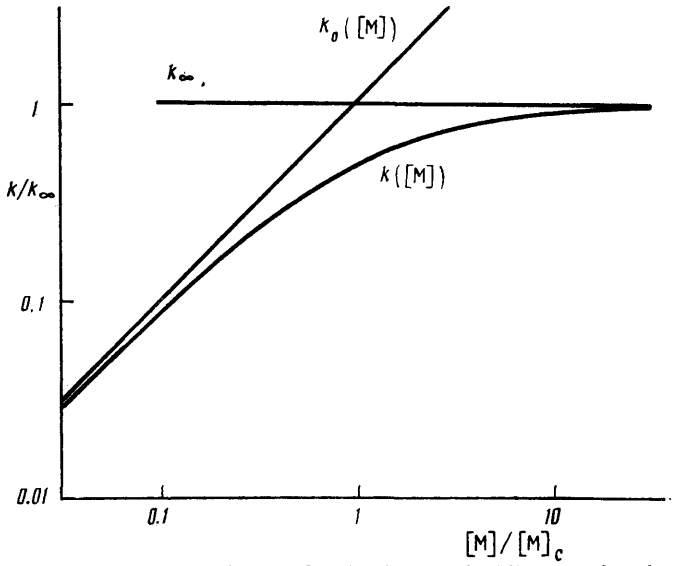


Figure 1. The reduced curve for the decrease in k/k_∞ as a function of $[M]/[M]_c$.

The dependence of k_0 and k_∞ on the temperature T has the form of a power function: $K \propto T^{-n}$ (except in cases with an appreciable energy barrier). This form of the temperature variation has therefore been used because it frequently yields a better agreement with experimental data over a wide temperature range than the Arrhenius law. The dependence of k_0 on the nature of the third species is usually reflected in the relative efficiencies of M_1 and M_2:

$$\{k_0(M_1)/[M_1]\} : \{k_0(M_2)/[M_2]\}.$$

Several thermal dissociation reactions of interest have been examined similarly to recombination reactions with pseudo-first order constants $k(M)$. The rate constants, expressed in s^{-1}, are designated in the Tables by the symbols k_0/s^{-1} and k_∞/s^{-1}. The multiplier F_c has the same significance in recombination and dissociation reactions.

Table 2. Compilation of data for reactions and the recommended rate constants.

Reaction	k_{298}, $cm^3\ s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3\ s^{-1}$	Temperatures range, K	$\Delta (E/R)$, K
		O_x reactions			
$O+O_2+M \rightarrow O_3+M$	$6.2\cdot10^{-34}$ $[O_2]$ (k_0)	±0.1	$6.2\cdot10^{-34}(T/300)^{-2}[O_2]$	200—300	$\Delta n=\pm0.5$
	$5.7\cdot10^{-33}$ $[N_2]$ (k_0)	±0.1	$5.7\cdot10^{-34}(T/300)^{-2.8}[N_2]$	200—300	$\Delta n=\pm0.5$
	$2.8\cdot10^{-12}$ (k_∞)	±0.2	$2.8\cdot10^{-12}$	200—300	$\Delta n=\pm0.5$
	$F_c=0,65$	$\Delta F_c=\pm0,1$	$F_c=\exp(-T/696)$	200—300	—
$O+O_2 \rightarrow O_3^*$	see Ref.9				
$O_3^*+M \rightarrow O_3+M$	see Ref.9				
$O+O_3 \rightarrow 2O_2$	$8.0\cdot10^{-15}$	±0.08	$8.0\cdot10^{-12}\exp(-2060/T)$	220—400	±200
$O+O_3 \rightarrow$ products	$1.5\cdot10^{-11}$	±0.5	—	—	—
$O(^1D)+O_2 \rightarrow O(^3P)+O_2$	$4.0\cdot10^{-11}$	±0.1	$3.2\cdot10^{-11}\exp(+67/T)$	200—350	±100
$O(^1D)+O_3 \rightarrow O_2+2O(^3P)$	$1.2\cdot10^{-10}$	±0.1	$1.2\cdot10^{-10}$	100—400	±100
$\rightarrow 2O_2(^3\Sigma_g^-)$	$1.2\cdot10^{-10}$	±0.1	$1.2\cdot10^{-10}$	100—400	±100
$O_2^*+O_3 \rightarrow$	see Ref.9				
$O_2(^1\Delta g)+M \rightarrow O_2(^3\Sigma_g^-)+M$	$1.6\cdot10^{-18}$ $(M=O_2)$	±0.2	$3.0\cdot10^{-18}\exp(-200/T)$	100—450	±200
	$\leqslant1.4\cdot10^{-19}$ $(M=N_2)$	—	—	—	—
	$5\cdot10^{-18}$ $(M=H_2O)$	±0.3	—	—	—
	$\leqslant2\cdot10^{-20}$ $(M=CO_2)$	—	—	—	—
$O_2(^1\Sigma_g^+)+M \rightarrow O_2(^3\Sigma_g^-)+M$	$8.0\cdot10^{-14}$ $(M=O)$	±0.3	—	—	—
	$4.0\cdot10^{-17}$ $(M=O_2)$	±0.3	—	—	—
	$2.0\cdot10^{-15}$ $(M=N_2)$	±0.1	$2.0\cdot10^{-15}$	200—300	±200
	$4.0\cdot10^{-12}$ $(M=H_2O)$	±0.3	—	—	—
	$4.1\cdot10^{-13}$ $(M=CO_2)$	±0.1	$4.1\cdot10^{-13}$	245—350	±200
$O_2(^1\Sigma_g^+)+O_3 \rightarrow$ products	$2.2\cdot10^{-11}$ —	±0.06	$2.2\cdot10^{-11}$	295—360	±300
$O_2(^1\Sigma_g^+)+O_3 \rightarrow O_2(^3\Sigma_g^-)+O_2$	see Ref.9				
$O_2+h\nu \rightarrow$ products	see Ref.9				
$O_3+h\nu \rightarrow$ products	see Ref.9				
		HO_x reactions			
$H+HO_2 \rightarrow H_2+O_2$	$5.6\cdot10^{-12}$ —	±0.5	$5.6\cdot10^{-12}$	245—300	±200
$\rightarrow 2HO$	$7.2\cdot10^{-11}$ —	±0.1	$7.2\cdot10^{-11}$	245—300	±200
$\rightarrow H_2O+O$	$2.4\cdot10^{-12}$ —	±0.5	$2.4\cdot10^{-12}$	245—300	±200
$H+O_2+M \rightarrow HO_2+M$	$5.9\cdot10^{-32}$ $[O_2]$ (k_0)	±0.1	$5.9\cdot10^{-32}(T/300)^{-1.0}[O_2]$	200—300	$\Delta n=\pm0.6$
	$5.9\cdot10^{-32}$ $[N_2]$ (k_0)	±0.1	$5.9\cdot10^{-32}(T/300)^{-1.0}[N_2]$	200—300	$\Delta n=\pm0.6$
	$7.5\cdot10^{-11}$ (k_∞)	±0.2	$7.5\cdot10^{-11}(T/300)^{+0.6}$	200—300	$\Delta n=\pm0.6$
	$F_c=0,55$	$\Delta F_c=\pm0,15$	$F_c=\exp(-T/502)$	200—300	—
$H+O_3 \rightarrow HO+O_2$	$2.8\cdot10^{-11}$	±0.2	$1.4\cdot10^{-10}\exp(-480/T)$	220—360	±100
$H+O_2 \rightarrow HO^*+O_2$	see Ref.9				
$O+H_2 \rightarrow HO+H$	$9\cdot10^{-18}$	±0.2	—	—	—
$O+HO \rightarrow O_2+H$	$3.3\cdot10^{-11}$	±0.1	$2.3\cdot10^{-11}\exp(+110/T)$	220—500	±100
$O+HO_2 \rightarrow HO+O_2$	$5.7\cdot10^{-11}$	±0.08	$2.9\cdot10^{-11}\exp(+200/T)$	200—400	±100
$O+H_2O_2 \rightarrow HO+HO_2$	$1.7\cdot10^{-15}$	±0.3	$1.4\cdot10^{-12}\exp(-2000/T)$	250—390	±1000
$O(^1D)+H_2 \rightarrow HO+H$	$1.1\cdot10^{-10}$	±0.1	$1.1\cdot10^{-10}$	200—350	±100
$O(^1D)+H_2O \rightarrow 2HO$	$2.3\cdot10^{-10}$	±0.1	$2.3\cdot10^{-10}$	200—350	±100
$HO+H_2 \rightarrow H_2O+H$	$6.7\cdot10^{-15}$	±0.1	$7.7\cdot10^{-12}\exp(-2100/T)$	200—450	±200
$HO+H_2(v=1)=H_2O+H$	$8.7\cdot10^{-13}$	±0.3	—	—	—
$HO+HO \rightarrow H_2O+O$	$1.8\cdot10^{-12}$	±0.15	—	—	—
$HO+HO+M \rightarrow H_2O_2+M$	$6.9\cdot10^{-31}$ $[O_2]$ (k_0)	±0.5	$6.9\cdot10^{-31}(T/300)^{-0.8}[O_2]$	200—300	$\Delta n=^{+2}_{-0.8}$
	$6.9\cdot10^{-31}$ $[N_2]$ (k_0)	±0.5	$6.9\cdot10^{-31}(T/300)^{-0.8}[N_2]$	200—300	$\Delta n=^{+2}_{-0.8}$
	$3.0\cdot10^{-11}$ (k_∞)	±0.5	$3.0\cdot10^{-11}$	200—300	$\Delta n=\pm0.5$
	$F_c=0,72$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/913)$	200—300	—
$HO+HO_2 \rightarrow H_2O+O_2$	$1.1\cdot10^{-10}$	±0.1	$4.8\cdot10^{-11}\exp(+250/T)$	250—400	±200
$HO+H_2O_2 \rightarrow H_2O+HO_2$	$1.7\cdot10^{-12}$	±0.1	$2.9\cdot10^{-12}\exp(-160/T)$	240—460	±100
$HO+O_3 \rightarrow HO_2+O_2$	$6.7\cdot10^{-14}$	±0.15	$1.9\cdot10^{-12}\exp(-1000/T)$	220—450	±300
$HO^*+M \rightarrow HO+M$	see Ref.9				
$HO^*+O_3 \rightarrow$ products	see Ref.9				
$HO_2+HO_2 \rightarrow H_2O_2+O_2$	$1.6\cdot10^{-12}$	±0.15	$2.2\cdot10^{-13}\exp(+600/T)$	230—420	±200
$HO_2+HO_2+M \rightarrow H_2O_2+O_2+M$	$4.5\cdot19^{-32}$ $[O_2]$	±0.15	—	—	—
	$5.2\cdot10^{-32}$ $[N_2]$	±0.15	$1.9\cdot10^{-33}\exp(+980/T)$ $[N_2]$	230—420	±300
	influence of H_2O, see Ref.9				
$HO_2+O_3 \rightarrow HO+2O_2$	$2.0\cdot10^{-15}$	±0.2	$1.4\cdot10^{-14}\exp(-600/T)$	250—350	$+500$ -100
$H_2O+h\nu \rightarrow HO+H$	see Ref.9				
$H_2O_2+h\nu \rightarrow 2HO$	see Ref.9				

Table 2 (cont'd.)

Reaction	k_{298}, $cm^3\ s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3\ s^{-1}$	Temperatures range, K	$\Delta (E/R)$, K
		NO_x reactions			
$O+NO+M \rightarrow NO_2+M$	$8.6\cdot10^{-32}$ $[O_2]$ (k_0)	±0.2	$8.6\cdot11^{-32}(T/300)^{-1.6}[O_2]$	200—300	$\Delta n=\pm0.5$
	$1.0\cdot10^{-31}$ $[N_2]$ (k_0)	±0.1	$1.0\cdot10^{-31}(T/300)^{-1.6}[N_2]$	200—300	$\Delta n=\pm0.5$
	$3.0\cdot10^{-11}$ (k_∞)	±0.2	$3.0\cdot10^{-11}(T/300)^{+0,3}$	300—1500	$\Delta n=\pm0.5$
	$F_c=0.85$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/1850)$	200—300	—
$O+NO_2 \rightarrow O_2+NO$	$9.7\cdot10^{-12}$	±0.06	$6.5\cdot10^{-12}\exp(+120/T)$	230—350	±120
$O+NO_2+M \rightarrow NO_3+M$	$9\cdot10^{-32}$ $[O_2]$ (k_0)	±0.3	$9\cdot10^{-32}(T/300)^{-2.0}[O_2]$	200—400	$\Delta n=\pm1.0$
	$9\cdot10^{-32}$ $[N_2]$ (k_0)	±0.1	$9\cdot10^{-32}(T/300)^{-2.0}[N_2]$	200—400	$\Delta n=\pm1.0$
	$2.2\cdot10^{-11}$ (k_∞)	±0.1	$2.2\cdot10^{-11}$	200—400	$\Delta n=\pm0.5$
	$F_c=0,8$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/1300)$	200—400	—
$O+NO_3 \rightarrow O_2+NO_2$	$1\cdot10^{-11}$	±0.5	—	—	—
$O+N_2O_5 \rightarrow$ products	$\leqslant3\cdot10^{-16}$	—	$\leqslant3\cdot10^{-16}$	220—300	—
$O(^1D)+N_2 \rightarrow O(^3P)+N_2$	$2.6\cdot10^{-11}$	±0.1	$1.8\cdot10^{-11}\exp(+107/T)$	200—350	±100
$O(^1D)+N_2O \rightarrow N_2+O_2$	$4.4\cdot10^{-11}$	±0.15	$4.4\cdot10^{-11}$	200—350	±100
$\rightarrow 2NO$	$7.2\cdot10^{-11}$	±0.15	$7.2\cdot10^{-11}$	200—350	±100
$N+HO \rightarrow NO+H$	$4.9\cdot10^{-11}$	±0.15	$3.8\cdot10^{-11}\exp(+85/T)$	250—500	±100
$N+O_2 \rightarrow NO+O$	$8.9\cdot10^{-17}$	±0.1	$4.4\cdot10^{-12}\exp(-3220/T)$	280—333	±350
$N+O_2(^1\Delta_g) \rightarrow NO+O$	$\leqslant1\cdot10^{-16}$	—	$\leqslant1\cdot10^{-16}$	200—300	—
$N+O_3 \rightarrow NO+O_2$	$1\cdot10^{-16}$	±0.3	—	—	—
$N+NO \rightarrow N_2+O$	$3.1\cdot10^{-11}$	±0.15	$3.1\cdot10^{-11}$	200—400	±100
$N+NO_2 \rightarrow N_2O+O$	$3.0\cdot10^{-12}$	±0.2	—	—	—
$HO+NH_3 \rightarrow H_2O+NH_2$	$1.6\cdot10^{-12}$	±0.15	$3.5\cdot10^{-12}\exp(-925/T)$	230—450	±200
$HO+HONO \rightarrow H_2O+NO_2$	$4.9\cdot10^{-12}$	±0.3	$1.8\cdot10^{-11}\exp(-390/T)$	280—340	±400
$HO+HONO_2 \rightarrow H_2O+NO_3$	$1.5\cdot10^{-13}$ (1 atm)	±0.1	see Ref.9		
$HO+HO_2NO_2 \rightarrow$ products	$5.0\cdot10^{-12}$	±0.2	$1.5\cdot10^{-12}\exp(+360/T)$	240—340	$+300$ -600
$HO+NO+M \rightarrow HONO+M$	$7.4\cdot10^{-31}$ $[O_2]$ (k_0)	±0.2	$7.4\cdot10^{-31}(T/300)^{-2.4}[O_2]$	200—440	$\Delta n=\pm1.0$
	$7.4\cdot10^{-31}$ $[N_2]$ (k_0)	±0.1	$7.4\cdot10^{-31}(T/300)^{-2.4}[N_2]$	200—440	$\Delta n=\pm0.5$
	$1.0\cdot10^{-11}$ (k_∞)	±0.2	$1.0\cdot10^{-11}$	200—400	$\Delta n=\pm0.5$
	$F_c=0,8$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/1300)$	200—400	—
$HO+NO_2+M \rightarrow HONO_2+M$	$2.2\cdot10^{-30}$ $[O_2]$ (k_0)	±0.1	$2.2\cdot10^{-30}(T/300)^{-2.9}[O_2]$	200—300	$\Delta n=\pm0.5$
	$2.6\cdot10^{-30}$ $[N_2]$ (k_0)	±0.1	$2.6\cdot10^{-30}(T/300)^{-2.9}[N_2]$	200—300	$\Delta n=\pm0.5$
	$5.2\cdot10^{-11}$ (k_∞)	±0.2	$5.2\cdot10^{-11}$	200—300	$\Delta n=\pm0.5$
	$F_c=0,43$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/353)$	200—300	—
$HO+NO_3 \rightarrow HO_2+NO_2$	$2.3\cdot10^{-11}$	±0.2	—	—	—
$HO_2+NO \rightarrow HO+NO_2$	$8.3\cdot10^{-12}$	±0.1	$3.7\cdot10^{-12}\exp(+240/T)$	230—500	±100
$HO_2+NO_2+M \rightarrow HO_2NO_2+M$	$1.5\cdot10^{-31}$ $[O_2]$ (k_0)	±0.1	$1.5\cdot10^{-31}(T/300)^{-3/2}[O_2]$	220—360	$\Delta n=\pm1$
	$1.8\cdot10^{-31}$ $[N_2]$ (k_0)	±0.1	$1.8\cdot10^{-31}(T/300)^{-3/2}[N_2]$	220—360	$\Delta n=\pm1$
	$4.7\cdot10^{-12}$ (k_∞)	±0.1	$4.7\cdot10^{-12}$	200—300	$\Delta n=\pm1$
	$F_c=0.6$	$\Delta F_c=\pm0.1$	see Ref.9		
$HO_2NO_2+M \rightarrow HO_2+NO_2+M$	$9.3\cdot10^{-21}$ $[O_2]$ (k_0/s^{-1})	±0.3	$3.6\cdot10^{-6}\exp(-10\,000/T)[O_2]\ c^{-1}$	260—300	±500
	$1.3\cdot10^{-20}$ $[N_2]$ (k_0/s^{-1})	±0.3	$5\cdot10^{-6}\exp(-10\,000/T)[N_2]\ c^{-1}$	260—300	±500
	0.23 (k_∞/c^{-1})	±0.6	$3.4\cdot10^{14}\exp(-10420/T)\ c^{-1}$	250—300	±500
	$F_c=0,6$	$\Delta F_c=\pm0.1$	—	—	—
$HO_2+NO_3 \rightarrow O_2+NONO_2$ / $HO+NO_2+O_2$	$4.3\cdot10^{-12}$	±0.2	—	—	—
$NH_2+HO \rightarrow$ products	no recommended value see Ref.9				
$NH_2+HO_2 \rightarrow$ products	$3.4\cdot10^{-11}$	±0.4	—	—	—
$NH_2+O_2 \rightarrow$ products	$<3\cdot10^{-18}$				
$NH_2+O_3 \rightarrow$ products	$1.7\cdot10^{-13}$	±0.5	$4.9\cdot10^{-12}\exp(-1000/T)$	250—380	±500
$NH_2+NO \rightarrow$ products	$1.6\cdot10^{-11}$	±0.3	$1.6\cdot10^{-11}(T/298)^{-1.5}$	210—500	$\Delta n=\pm0.5$
$NH_2+NO_2 \rightarrow$ products	$1.9\cdot10^{-11}$	±0.3	$1.9\cdot10^{-11}(T/298)^{-2.2}$	250—500	$\Delta n=\pm1.5$
$2NO+O_2 \rightarrow 2NO_2$	$2.0\cdot10^{-38}$	±0.1	$3.3\cdot10^{-39}\exp(+530/T)$	273—600	±400
$NO+O_3 \rightarrow NO_2+O_2$	$1.8\cdot10^{-14}$	±0.08	$1.8\cdot10^{-12}\exp(-1370/T)$	195—304	±200
$NO+NO_3 \rightarrow 2NO_2$	$2.7\cdot10^{-11}$	±0.12	$1.6\cdot10^{-11}\exp(+150/T)$	200—300	±100
$NO_2+O_3 \rightarrow NO_3+O_2$	$3.2\cdot10^{-17}$	±0.06	$1.2\cdot10^{-13}\exp(-2450/T)$	230—360	±150
$NO_2+NO_3+M \rightarrow N_2O_5+M$	$2.7\cdot10^{-30}$ $[N_2]$ (k_0)	±0.1	$2.7\cdot10^{-30}(T/300)^{-3.4}[N_2]$	200—300	$\Delta n=\pm0.5$
	$2.0\cdot10^{-12}$ (k_∞)	±0.1	$2.0\cdot10^{-12}(T/300)^{+0.2}$	200—500	$\Delta n=\pm0.6$
	$F_c=0.34$				
$N_2O_5+M \rightarrow NO_2+NO_3+M$	$1.6\cdot10^{-19}$ $[N_2]$ (k_0/s^{-1})	±0.2	$2.2\cdot10^{-3}(T/300)^{-4.4}\exp(-11080/T)$. $[N_2]\ s^{-1}$	200—300	±500
	$6.9\cdot10^{-2}$ (k_∞/s^{-1})	±0.3	$9.7\cdot10^{14}(T/300)^{+0.1}\exp(-11080/T)\ c^{-1}$	200—300	±500
	$F_c=0.34$	—	—	—	—

Table 2 (cont'd.)

Reaction	k_{298}, $cm^3\ s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3\ s^{-1}$	Temperatures range, K	$\Delta (E/R)$, K
		NO_x reactions			
$N_2O_5 \rightleftarrows NO_2+NO_3$	see Ref.9				
$N_2O_5+H_2O \rightarrow 2HONO_2$	$<2\cdot10^{-21}$	—	—	—	—
$HONO+h\nu \rightarrow$ products	see Ref.9				
$HONO_2+h\nu \rightarrow$ products	see Ref.9				
$HO_2NO_2+h\nu \rightarrow$ products	see Ref.9				
$NO+h\nu \rightarrow$ products	see Ref.9				
$NO_2+h\nu \rightarrow$ products	see Ref.9				
$NO_3+h\nu \rightarrow$ products	see Ref.9				
$N_2O+h\nu \rightarrow$ products	see Ref.9				
$N_2O_5+h\nu \rightarrow$ products	see Ref.9				
		Organic reactions			
$O+CH_3 \rightarrow HCHO+H$	$1.4\cdot10^{-10}$	±0.1	$1.4\cdot10^{-10}$	200—900	±100
$O+CN \rightarrow CO+N(^2D)$	$1.4\cdot10^{-11}$	±0.2	—	—	—
$\rightarrow CO+N(^4S)$	$3.4\cdot10^{-12}$	±0.2	—	—	—
$O(^1D)+CH_4 \rightarrow HO+CH_3$	$1.4\cdot10^{-10}$	±0.1	$1.4\cdot10^{-10}$	200—300	±100
$\rightarrow HCHO+H_2$	$1.5\cdot10^{-11}$	±0.1	$1.5\cdot10^{-11}$	200—300	±100
$HO+CH_4 \rightarrow H_2O+CH_3$	$8.3\cdot10^{-15}$	±0.1	$3.7\cdot10^{-12}\exp(-1820/T)$	240—300	±100
$HO+C_2H_2+M \rightarrow C_2H_2OH+M$	$5\cdot10^{-30}\ [N_2]\ (k_0)$	±0.1	$5\cdot10^{-30}\ [N_2]$	220—300	$\Delta n=\pm1$
	$8.3\cdot10^{-13}\ (k_\infty)$	±0.1	$8.3\cdot10^{-13}\ (T/300)^{+2}$	220—300	$\Delta n=\pm1$
	$F_c=0,6$	$\Delta F_c=\pm0.2$	—	—	—
$HO+C_2H_4+M \rightarrow C_2H_4OH+M$	$9.5\cdot10^{-29}\ [O_2]\ (k_0)$	±0.3	$9.5\cdot10^{-29}\ (T/300)^{-3.1}[O_2]$	200—300	$\Delta n=\pm2$
	$9.5\cdot10^{-29}\ [N_2]\ (k_0)$	±0.3	$9.5\cdot10^{-29}\ (T/300)^{-3.1}[N_2]$	200—300	$\Delta n=\pm2$
	$9\cdot10^{-12}\ (k_\infty)$	±0.3	$9\cdot10^{-12}$	200—300	$\Delta n=\pm1$
	$F_c=0.7$	$\Delta F_c=0.2$	$F_c=\exp(-T/840)$	200—300	—
$HO+C_2H_6 \rightarrow H_2O+C_2H_5$	$2.7\cdot10^{-13}$	±0.1	$7.4\cdot10^{-12}\exp(-990/T)$	230—300	±100
$HO+C_3H_6+M \rightarrow C_3H_6OH+M$	$8\cdot10^{-27}\ [O_2]\ (k_0)$	±1	$8\cdot10^{-27}(T/300)^{-3.5}[O_2]$	200—300	$\Delta n=\pm1$
	$8\cdot10^{-27}\ [N_2]\ (k_0)$	±1	$8\cdot10^{-27}\ (T/300)^{-3.5}[N_2]$	200—300	$\Delta n=\pm1$
	$3.0\cdot10^{-11}\ (k_\infty)$	±0.1	$3.0\cdot10^{-11}$	200—300	$\Delta n=\pm1$
	$F_c=0.5$	$\Delta F_c=\pm0.2$	$F_c=\exp(-T/433)$	—	—
$HO+C_3H_8 \rightarrow H_2O+C_3H_7$	$1.1\cdot10^{-12}$	±0.15	$8.6\cdot10^{-12}\ (-610/T)$	~300	±200
$HO+CO \rightarrow H+CO_2$	$(1.5.10^{-13}).[1+0.6(P/atm)]$ (0—760 mmHg, air)	±0.1	$(1.5.10^{-13})[1+0.6(P/atm)]$ (0—760 mmHg, air)	200—300	±300
$HO+HCHO \rightarrow H_2O+HCO$	$1.1\cdot10^{-11}$	±0.1	$1.6\cdot10^{-11}\exp(-110/T)$	230—580	±150
$HO+CH_3CHO \rightarrow H_2O+CH_3CO$	$1.6\cdot10^{-11}$	±0.1	$5.6\cdot10^{-12}\exp(+310/T)$	240—530	±200
$HO+C_2H_5CHO \rightarrow$ products	$2.0\cdot10^{-11}$	±0.15	—	—	—
$HO+(CHO)_2 \rightarrow$ products	$1.1\cdot10^{-11}$	±0.3	—	—	—
$HO+HOCH_2CHO \rightarrow H_2O+HOCH_2CO$	$8.0\cdot10^{-12}$	±0.3	—	—	—
$\rightarrow H_2O+HOCHCHO$	$2.0\cdot10^{-12}$	±0.3	—	—	—
$HO+CH_3COCHO \rightarrow H_2O+CH_3COCO$	$1.7\cdot10^{-11}$	±0.3	—	—	—
$HO+CH_3COCH_3 \rightarrow H_2O+CH_2COCH_3$	$2.3\cdot10^{-13}$	±0.2	$1.7\cdot10^{-12}\exp(-600/T)$	240—440	±300
$HO+CH_3OH \rightarrow H_2O+CH_2OH$	$9.0\cdot10^{-13}$	±0.2	$9.1\cdot10^{-12}\exp(-690/T)$	240—1000	±250
$\rightarrow H_2O+CH_3O$					
$HO+C_2H_5OH \rightarrow$ products	$3.4\cdot10^{-12}$	±0.2	$9.3\cdot10^{-12}\exp(-300/T)$	250—450	±200
$HO+n\text{-}C_3H_7OH \rightarrow$ products	$5.3\cdot10^{-12}$	±0.2			
$HO+iso\text{-}C_3H_7OH \rightarrow$ products	$5.6\cdot10^{-12}$	±0.2	$5.6\cdot10^{-12}$	240—440	±200
$HO+CH_3OOH \rightarrow H_2O+CH_2OOH$	$4.4\cdot10^{-12}$	±0.3	—	—	—
$\rightarrow H_2O+CH_3OO$	$6.6\cdot10^{-12}$	±0.3	—	—	—
$HO+HCOOH \rightarrow$ products	$4.8\cdot10^{-13}$	±0.2	$4.8\cdot10^{-13}$	290—430	±150
$HO+CH_3COOH \rightarrow$ products	$7.4\cdot10^{-13}$	±0.3	$1.3\cdot10^{-12}\exp(-170/T)$	290—440	±300
$HO+CH_3CO_3NO_2 \rightarrow$ products	$1.4\cdot10^{-13}$	±0.2	$1.2\cdot10^{-12}\exp(-650/T)$	270—300	±400
$HO+HCN \rightarrow$ products	3.10^{-14} (1 atm)	±0.5	$1.2.10^{-13}\exp(-400/T)$(1 atm)	296—433	±300
$HO+CH_3CN \rightarrow$ products	$2.0\cdot10^{-14}$	±0.2	$6.3\cdot10^{-13}\exp(-1030/T)$	250—360	±250
$HO_2+CH_3O_2 \rightarrow O_2+CH_3O_2H$	$4.9\cdot10^{-12}$	±0.3	$1.7\cdot10^{-13}\exp(+1000/T)$	250—380	±500
$HO_2+C_2H_5O_2 \rightarrow O_2+C_2H_5O_2H$	$5.8\cdot10^{-12}$	±0.2	$6.5\cdot10^{-13}\exp(+650/T)$	240—380	±200
$HO_2+HCHO \rightarrow HOCH_2OO$	$7.9\cdot10^{-14}$	±0.2	$9.7\cdot10^{-15}\exp(+625/T)$	220—420	±600
$HOCH_2OO \rightarrow HO_2+HCHO$	$1.5\cdot10^{2}\ c^{-1}$	±0.2	$2.4\cdot10^{12}\exp(-7000/T)$	220—420	±1000
$NO_3+C_2H_2 \rightarrow$ products	$<1\cdot10^{-16}$	—	—	—	—
$NO_3+C_2H_4 \rightarrow$ products	$2.1\cdot10^{-16}$	±0.3	—	—	—
$NO_3+C_3H_6 \rightarrow$ products	$9.4\cdot10^{-15}$	±0.2	—	—	—
$NO_3+HCHO \rightarrow HNO_3+HCO$	$6\cdot10^{-16}$	±0.3	—	—	—
$NO_3+CH_3CHO \rightarrow HNO_3+CH_3CO$	$2.7\cdot10^{-15}$	±0.2	$1.4\cdot10^{-12}\exp(-1860/T)$	260—370	±500
$NO_3+CH_3OH \rightarrow$ products	$<1\cdot10^{-15}$	—	—	—	—
$NO_3+C_2H_5OH \rightarrow$ products	$<2\cdot10^{-15}$	—	—	—	—
$NO_3+iso\text{-}C_3H_7OH \rightarrow$ products	$<5\cdot10^{-15}$	—	—	—	—
$CH_3+O_2+M \rightarrow CH_3O_2+M$	$8\cdot10^{-31}\ [N_2]\ (k_0)$	±0.2	$8\cdot10^{-31}\ (T/300)^{-3.3}[N_2]$	200—600	$\Delta n=\pm1$
	$2.2\cdot10^{-12}\ (k_\infty)$	±0.3	$2.2\cdot10^{-12}\ (T/300)^{1}$	200—400	$\Delta n=\pm1$
	$F_c=0.27$ —	$\Delta F_c=\pm0.1$			
$C_2H_5+O_2 \rightarrow C_2H_4+HO_2$	$<2\cdot10^{-15}$ —	—	$1.4\cdot10^{-12}\exp(-1950/T)$	300—2500	±600

Table 2 (cont'd.)

Reaction	k_{298}, cm^3 s^{-1}	$\Delta \lg k_{298}$	Temperature dependence of K, cm^3 s^{-1}	Temperatures range, K	$\Delta(E/R)$, K
	Organic reactions				
$C_2H_5+O_2+M\rightarrow C_2H_5O_2+M$	$2.0\cdot10^{-28}$ [O_2] (k_0)	±0.3	$2.0\cdot10^{-28}$ $(T/300)^{-3.8}$[O_2]	200—300	$\Delta n=\pm1$
	$2.0\cdot10^{-28}$ [N_2] (k_0)	±0.3	$2.0\cdot10^{-28}$ $(T/300)^{-3.8}$[N_2]	200—300	$\Delta n=\pm1$
	$5.0\cdot10^{-12}$ (k_∞)	±0.3	$5\cdot10^{-12}$	200—300	$\Delta n=\pm1$
	$F_c=0.7$	$\Delta F_c=\pm0.2$	$F_c=\exp(-T/840)$	—	—
n-$C_3H_7+O_2+M\rightarrow n$-$C_3H_7O_2+M	$6\cdot10^{-12}$ (k_∞)	±0.3	$6\cdot10^{-12}$	200—300	$\Delta n=\pm1$
iso-$C_3H_7+O_2+M\rightarrow$ iso-$C_3H_7O_2+M$	$1.5\cdot10^{-11}$ (k_∞)	±0.3	$1.5\cdot10^{-11}$	200—300	$\Delta n=\pm1$
$HCO+O_2\rightarrow CO+HO_2$	$5.6\cdot10^{-12}$	±0.2	$3.5\cdot10^{-12}\exp(+140/T)$	300—500	±150
$CH_3CO+O_2(+M)\rightarrow CH_3CO(+M)$	2.10^{12} (1 – mmHg)	—	—	—	—
	$5\cdot10^{-12}$ (k_∞)	±0.5	$5\cdot10^{-12}$	200—300	$\Delta n=\pm1$
$CH_3O+O_2\rightarrow HCHO+HO_2$	$1.9\cdot10^{-15}$	±0.2	$7.2\cdot10^{-14}\exp(-1080/T)$	298—610	±300
$C_2H_5O+O_2\rightarrow CH_3CHO+HO_2$	$8.0\cdot10^{-15}$	±0.3	—	—	—
n-$C_3H_7O+O_2\rightarrow C_2H_5CHO+HO_2$	$8\cdot10^{-15}$	±0.5	—	—	—
iso-$C_3H_7O+O_2\rightarrow CH_3COCH_3+HO_2$	$8\cdot10^{-15}$	±0.3	$1.5\cdot10^{-14}\exp(-200/T)$	290—390	±200
$CH_2OH+O_2\rightarrow HCHO+HO_2$	$9.8\cdot10^{-12}$	±0.15	—	—	—
$CH_3+O_3\rightarrow$products	$2.5\cdot10^{-12}$	±0.3	$5.1\cdot10^{-12}\exp(-210/T)$	240—400	±200
$CH_3O+NO+M\rightarrow CH_3ONO+M$	$3\cdot10^{-28}$ [He] (k_0)	±0.5	—	—	—
	$6\cdot10^{-28}$ [N_2] (k_0)	±0.5	—	—	—
	$2\cdot10^{-11}$ (k_∞)	±0.3	$2\cdot10^{-11}$	200—400	—
	$F_c=0.6$	—	—	—	—
$RO+NO+M\rightarrow RONO+M$	**see Ref.9**				
$RO+NO\rightarrow R'O+HNO$	**see Ref.9**				
$CH_3CH_2O+NO_2+M\rightarrow CH_3ONO_2+M$	$2.6\cdot10^{-29}$ [He] (k_0)	±0.5	$2.6\cdot10^{-29}$ $(T/300)^{-4.5}$[He]	200—400	$\Delta n=\pm2$
	$1.5\cdot10^{-11}$ (k_∞)	±0.3	$1.5\cdot10^{-11}$	300—400	—
	$F_c=0.4$	—	—	—	—
$CH_3O+NO_2\rightarrow HCHO+HONO$	$<3\cdot10^{-13}$	—	$<3\cdot10^{-13}$	200—300	—
$RO+NO_2+M\rightarrow RONO_2+M$	**see Ref.9**				
$RO+NO_2\rightarrow R'O+HONO$	**see Ref.9**				
$CH_3O_2+NO\rightarrow CH_3O+NO_2$	$7.6\cdot10^{-12}$	±0.1	$4.2\cdot10^{-12}\exp(+180/T)$	240—360	±180
$C_2H_5O_2+NO\rightarrow C_2H_5O+NO_2$	$8.8\cdot10^{-12}$	±0.3	—	—	—
$C_2H_5O_2+NO(+M)\rightarrow C_2H_5ONO_2(+M)$	$\leqslant1.3\cdot10^{-13}$	—	—	—	—
n-$C_3H_7O_2+NO\rightarrow n$-$C_3H_7O+NO_2$	$8.7\cdot10^{-12}$	±0.3	—	—	—
n-$C_3H_7O_2+NO(+M)\rightarrow n$-$C_3H_7ONO_2(+M)$	$1.8\cdot10^{-13}$	±0.3	—	—	—
iso-$C_3H_7O_2+NO\rightarrow$ iso-$C_3H_7O+NO_2$	$8.5\cdot10^{-12}$	±0.3	—	—	—
iso-$C_3H_7O_2+NO(+M)\rightarrow$ iso-$C_3H_7ONO_2(+M)$	$3.8\cdot10^{-13}$	±0.3	—	—	—
$CH_3CO_3+NO\rightarrow CH_3+CO_2+NO_2$	$1.4\cdot10^{-11}$	±0.7	—	—	—
$CH_3O_2+NO_2+M\rightarrow CH_3O_2NO_2+M$	$2.3\cdot10^{-30}$ [O_2] (k_0)	±0.2	$2.3\cdot10^{-30}$ $(T/300)^{-4.0}$[O_2]	200—300	$\Delta n=\pm2$
	$2.3\cdot10^{-30}$ [N_2] (k_0)	±0.1	$2.3\cdot10^{-30}$ $(T/300)^{-4.0}$[N_2]	200—300	$\Delta n=\pm2$
	$8.0\cdot10^{-12}$ (k_∞)	±0.2	$8\cdot10^{-12}$	200—300	$\Delta n=\pm0.5$
	$F_c=0.4$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/327)$		
$CH_3O_2NO_2+M\rightarrow CH_3O_2+NO_2+M$	**$6.8.10^{-19}$ [N_2](k_0/s^{-1})**	±0.3	**$9.10^{-5}\exp(-9690/T)$[N_2] s^{-1}**	250—300	±500
	4.5 (k_∞/s^{-1})	±0.3	**$1.1.10^{16}\exp(-10560/T)$ s^{-1}**	250—300	±500
	$F_c=0.4$				
$C_2H_5O_2+NO_2+M\rightarrow C_2H_5O_2NO_2+M$	$5\cdot10^{-12}$ (k_∞)	±0.5	$5\cdot10^{-12}$	200—300	$\Delta n=\pm1$
$C_2H_5O_2NO_2+M\rightarrow C_2H_5O_2+NO_2+M$	**no recommended value see Ref.9**				
$CH_3CO_3+NO_2+M\rightarrow CH_3CO_3NO_2+M$	$2\cdot10^{-28}$ [N_2] (k_0)	±0.5	—	—	—
	$8.4\cdot10^{-12}$ (k_∞)	±0.3	—	—	—
	$F_c=0.27$	—	—	—	—
$CH_3CO_3NO_2+M\rightarrow CH_3CO_3+NO_2+M$	**$1.5.10^{-20}$ [N_2] (k_0/s^{-1})**	±0.5	**$6.3.10^{-3}\exp(-12785/T)$ [N_2] s^{-1}**	300—320	±1000
	$5.8.10^{-4}$ (k_∞/s^{-1})	±0.3	**$2.2.10^{16}\exp(-13435/T)$ s^{-1}**	300—320	±500
	$F_c=0.27$				
$CH_3O_2+CH_3O_2\rightarrow CH_3OH+HCHO+O_2$	$\geqslant2.1\cdot10^{-13}$	±0.3	$1.7\cdot10^{-13}\exp(+220/T)$	200—400	±220
$\rightarrow 2CH_3O+O_2$	$1.3\cdot10^{-13}$	±0.3			
$\rightarrow CH_3OOCH_3+O_2$	$\leqslant3\cdot10^{-14}$	—	—	—	—
$CH_3O_2+CH_3CO_3\rightarrow CH_3O+CH_3CO_2+O_2$	$5.5\cdot10^{-12}$	±0.5	$2.2\cdot10^{-12}\exp(+490/T)$	250—370	±500
$\rightarrow CH_3CO_2H+HCHO+O_2$	$5.5\cdot10^{-12}$	±0.5			
$C_2H_5O_2+C_2H_5O_2\rightarrow C_2H_5OH+CH_3CHO+O_2$	$8.6\cdot10^{-14}$	±0.12	$1.2\cdot10^{-13}\exp(-110/T)$	250—450	$+300$ -100
$\rightarrow 2C_2H_5O+O_2$					
$\rightarrow C_2H_5OOC_2H_5+O_2$					
n-$C_3H_7O_2+n$-$C_3H_7O_2\rightarrow n$-$C_3H_7OH+C_2H_5CHO+O_2$	$3\cdot10^{-13}$	±0.5	—	—	—
n-$C_3H_7O_2+n$-$C_3H_7O_2\rightarrow 2n$-$C_3H_7O+O_2$					
iso-$C_3H_7O_2+$ iso-$C_3H_7O_2\rightarrow$ iso-$C_3H_7OH+CH_3COCH_3+O_2$	$4.4\cdot10^{-14}$	±0.3	$6.0\cdot10^{-14}\exp(-1460/T)$	300—400	±300
iso-$C_3H_7O_2+$ iso-$C_3H_7O_2\rightarrow 2$iso-$C_3H_7O+O_2$	$5.6\cdot10^{-14}$	±0.3	$3.2\cdot10^{-12}\exp(-2580/T)$	300—400	±300
	$1.6\cdot10^{-11}$	±0.5	$2.8\cdot10^{-12}\exp(+530/T)$	250—370	±500
$CH_3CO_3+CH_3CO_3\rightarrow 2CH_3CO_2+O_2$					
$RCHO+H_2O\rightarrow RCOOH+H_2O$	**no recommended value see Ref.9**				
$RCHO+NO_2\rightarrow RCHO+NO_3$					
$RCHO+SO_2\rightarrow$products					
$RCHO+HCHO\rightarrow$products					
$CN+O_2\rightarrow$products	$2.1\cdot10^{-11}$	±0.15	$1.1\cdot10^{-11}\exp(+205/T)$	290—760	±200
	$1\cdot10^{-20}$	±1.0			

Table 2 (cont'd.)

Reaction	k_{298}, $cm^3\ s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3\ s^{-1}$	Temperatures range, K	$\Delta (E/R)$, K
		Organic reactions			
$O_3+C_2H_2\rightarrow$products	$1.7\cdot10^{-18}$	±0.1	$1.2\cdot10^{-14}\exp(-2630/T)$	180—360	±100
$O_3+C_2H_4\rightarrow$products	$1.1\cdot10^{-17}$	±0.15	$1.3\cdot10^{-14}\exp(-2105/T)$	250—360	±400
$O_3+C_3H_6\rightarrow$products	see Ref.9				
$HCHO+h\nu\rightarrow$products	see Ref.9				
$CH_3CHO+h\nu\rightarrow$products	see Ref.9				
$C_2H_5CHO+h\nu\rightarrow$products	see Ref.9				
$(CHO)_2+h\nu\rightarrow$products	see Ref.9				
$CH_3COCHO+h\nu\rightarrow$products	see Ref.9				
$CH_3COCH_3+h\nu\rightarrow$products	see Ref.9				
$CH_3OOH+h\nu\rightarrow$products	see Ref.9				
$CH_3O_2NO_2+h\nu\rightarrow$products	see Ref.9				
$CH_3CO_3NO_2+h\nu\rightarrow$products	see Ref.9				
		SO_x reactions			
$O+H_2S\rightarrow HO+HS$	$2.2\cdot10^{-14}$	±0.3	$1.4\cdot10^{-11}\exp(-1920/T)$	290—500	±750
$O+CS\rightarrow CO+S$	$2.1\cdot10^{-11}$	±0.1	$2.7\cdot10^{-10}\exp(-760/T)$	150—300	±250
$O+CH_3SCH_3\rightarrow CH_3SO+CH_3$	$5.0\cdot10^{-11}$	±0.1	$1.3\cdot10^{-11}\exp(+409/T)$	270—560	±100
$O+CS_2\rightarrow SO+CS$	$3.6\cdot10^{-12}$	±0.2	$3.2\cdot10^{-11}\exp(-650/T)$	200—500	±100
$O+CH_3SSCH_3\rightarrow CH_3SO+CH_3S$	$1.3\cdot10^{-10}$	±0.3	$5.5\cdot10^{-11}\exp(+250/T)$	290—570	±100
$O+OCS\rightarrow SO+CO$	$1.4\cdot10^{-14}$	±0.2	$2.6\cdot10^{-11}\exp(-2250/T)$	220—600	±150
$O+SO_2+M\rightarrow SO_3+M$	$1.4\cdot10^{-33}\ [O_2]$ (k_0)	±0.3	$4.0\cdot10^{-32}\exp(-1000/T)[O_2]$	200—400	$+200$ -100
$O+SO_3+M\rightarrow SO_3+M$	$1.4\cdot10^{-33}\ [N_2]$ (k_0)	±0.3	$4.0\cdot10^{-32}\exp(-1000/T)[O_2]$	200—400	$+200$ -100
$S+O_2\rightarrow SO+O$	$2.3\cdot10^{-12}$	±0.2	$2.3\cdot10^{-12}$	230—400	±200
$S+O_3\rightarrow SO+O_2$	$1.2\cdot10^{-11}$	±0.3			
$HO+H_2S\rightarrow H_2O+HS$	$4.8\cdot10^{-12}$	±0.08	$6.3\cdot10^{-12}\exp(-80/T)$	200—300	$+80$
$HO+CH_3SH\rightarrow$products	$3.3\cdot10^{-11}$	±0.1	$9.9\cdot10^{-12}\exp(+356/T)$	240—430	±100
$HO+CH_3SCH_3\rightarrow H_2O+CH_2SCH_3$	$4.4\cdot10^{-12}$	±0.1	$9.6\cdot10^{-12}\exp(-234/T)$	250—400	±300
$\rightarrow CH_3S(OH)CH_3$	$1.7\cdot10^{-12}$ (1 atm, air)	±0.3	см. [9]		
$HO+CS_2\rightarrow$products	$\leqslant7.0\cdot10^{-15}$ $([O_2]=0)$				
	$2.0\cdot10^{-12}$ (1 atm, air)	±0.3	$8.8\cdot10^{-16}\exp(+2300/T)$	260—300	±500
$HO+CH_3SSCH_3\rightarrow$products	$2.0\cdot10^{-10}$	±0.1	$6.0\cdot10^{-11}\exp(+380/T)$	250—370	±300
$HO+OCS\rightarrow$products	$2.0\cdot10^{-15}$	±0.3	$1.1\cdot10^{-13}\exp(-1200/T)$	250—500	±500
$HO+SO_2+M\rightarrow HOSO_2+M$	$5.0\cdot10^{-31}\ [O_2]$ (k_0)	±0.3	$5.0\cdot10^{-31}\ (T/300)^{-3,3}[O_2]$	200—300	$\Delta n=\pm0.5$
	$5.0\cdot10^{-31}\ [N_2]$ (k_0)	±0.3	$5.0\cdot10^{-31}\ (T/300)^{-3,3}[N_2]$	200—300	$\Delta n=\pm0.5$
	$2\cdot10^{-12}$ (k_∞)	±0.3	$2\cdot10^{-12}$	200—300	$\Delta n=\pm1$
	$F_c=0.45$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/380)$	200—300	—
$HOSO_2+O_2\rightarrow HO_2+SO_3$	$4.0\cdot10^{-13}$	±0.1	—	—	—
$HO_2+SO_2\rightarrow$products	$\leqslant1\cdot10^{-18}$	—	—	—	—
$NO_3+H_2H_2S\rightarrow$products	$<1\cdot10^{-15}$	—	—	—	—
$NO_3+CS_2\rightarrow$products	$<1\cdot10^{-15}$	—	—	—	—
$NO_3+OCS\rightarrow$products	$<3\cdot10^{-15}$	—	—	—	—
$NO_3+SO_2\rightarrow$products	$<1\cdot10^{-19}$	—	—	—	—
$NO_3+CH_3SH\rightarrow$products	$9.2\cdot10^{-13}$	±0.15	$9.2\cdot10^{-13}$	250—370	±400
$NO_3+CH_3SCH_3\rightarrow$products	$1.0\cdot10^{-12}$	±0.15	$1.9\cdot10^{-13}\exp(+500/T)$	250—380	±300
$NO_3+CH_3SSCH_3\rightarrow$products	$7\cdot10^{-13}$	±0.3	$7\cdot10^{-13}$	300—380	±500
$CH_3O_2+SO_2\rightarrow CH_3O+SO_3$	$<5\cdot10^{-17}$				
$\rightarrow CH_3O_2SO_2$	no recommended value see Ref.9				
$HS+O_2\rightarrow HO+SO$	$\leqslant4\cdot10^{-19}$	—	—	—	—
$HS+O_3\rightarrow HSO+O_2$	$3.6\cdot10^{-12}$	±0.2	—	—	—
$HS+NO+M\rightarrow HSNO+M$	$2.4\cdot10^{-31}\ [N_2]$ (k_0)	±0.3	$2.4\cdot10^{-31}\ (T/300)^{-2,5}[N_2]$	200—300	$\Delta n=\pm1$
	$2.7\cdot10^{-11}$ (k_∞)	±0.5	$2.7\cdot10^{-11}$	200—300	—
	$F_c=0,6$	—	—	—	—
$HS+NO_2\rightarrow HSO+NO$	$5.8\cdot10^{-11}$	±0.3	$2,6\cdot10^{-11}\exp(+240/T)$	220—450	$+200$
$HSO+O_2\rightarrow$products	$\leqslant2\cdot10^{-17}$	—	—	—	—
$HSO+O_3\rightarrow$products	$1.1\cdot10^{-13}$	±0.8	—	—	—
$HSO+NO\rightarrow$products	$\leqslant1\cdot10^{-15}$	—	—	—	—
$HSO+NO_2\rightarrow$products	$9.6\cdot10^{-12}$	±0.3	—	—	—
$HSO_2+O_2\rightarrow$products	$3\cdot10^{-13}$	±0.8	—	—	—
$SO+O_2\rightarrow SO_2+O$	$6.7\cdot10^{-17}$	±0.15	$1.4\cdot10^{-13}\exp(-2275/T)$	230—420	±500
$SO+O_3\rightarrow SO_2+O_2$	$8.9\cdot10^{-14}$	±0.1	$4.5\cdot10^{-12}\exp(-1170/T)$	230—420	±150
$SO+NO_2\rightarrow SO_2+NO$	$1.4\cdot10^{-11}$	±0.1	$1.4\cdot10^{-11}$	240—360	±100
$SO_3+H_2O\rightarrow$products	no recommended value see Ref.9				
$CS+O_2\rightarrow$products	no recommended value see Ref.9				
$O_3+CH_3SCH_3\rightarrow$products	$<1\cdot10^{-18}$	—	—	—	—
$OCS+h\nu\rightarrow$products	see Ref.9				
$CS_2+h\nu\rightarrow$products	see Ref.9				
$CH_3SSCH_3+h\nu\rightarrow$products	see Ref.9				

Table 2 (cont'd.)

Reaction	k_{298}, $cm^3\ s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3\ s^{-1}$	Temperatures range, K	$\Delta(E/R)$, K
		FO_x reactions			
$O+FO \rightarrow O_2+F$	$5\cdot10^{-11}$	±0.5	—	—	—
$O+FO_2 \rightarrow O_2+FO$	$5\cdot10^{-11}$	±0.7	—	—	—
$O(^1D)+HF \rightarrow HO+F$	$1\cdot10^{-10}$	±0.5	—	—	—
$O(^1D)+COF_2 \rightarrow CO_2+F_2$	$2.2\cdot10^{-11}$	±0.2	—	—	—
$\rightarrow O(^3P)+COF_2$	$5.2\cdot10^{-11}$	±0.2	—	—	—
$F+H_2 \rightarrow HF+H$	$2.8\cdot10^{-11}$	±0.1	$1.9\cdot10^{-10}\exp(-570/T)$	190—770	±150
$F+H_2O \rightarrow HF+HO$	$1.1\cdot10^{-11}$	±0.5	$4.2\cdot10^{-11}\exp(-400/T)$	240—370	±200
$F+O_2+M \rightarrow FO_2+M$	$4.3\cdot10^{-33}\ [N_2]$ (k_0)	±0.3	$4.3\cdot10^{-33}\ (T/300)^{-1.4}[N_2]$	200—300	$\Delta n=\pm1$
	$3\cdot10^{-11}$ (k_∞)	±0.5	$3\cdot10^{-11}$	200—300	$\Delta n=\pm1$
	$F_c=0.85$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/1850)$	200—300	—
$FO_2+M \rightarrow F+O_2+M$	$2.2.10^{-17}\ [N_2]$ (k_0/s^{-1})	±0.5	$6.3.10^{-9}\exp(-5800/T)\ [N_2]\ s^{-1}$	200—400	±1000
$F+O_3 \rightarrow FO+O_2$	$1.3\cdot10^{-11}$	±0.3	$2.8\cdot10^{-11}\exp(-226/T)$	250—365	±200
$F+NO_2+M \rightarrow FONO+M$	$1.0\cdot10^{-30}\ [O_2]$ (k_0)	±0.5	$1.0\cdot10^{-30}\ (T/300)^{-2.0}[O_2]$	200—300	$\Delta n=\pm1$
	$1.0\cdot10^{-30}\ [N_2]$ (k_0)	±0.5	$1.0\cdot10^{-30}\ (T/300)^{-2.0}[N_2]$	200—300	$\Delta n=\pm1$
	$2\cdot10^{-10}$ (k_∞)	±0.8	$2\cdot10^{-10}$	200—300	$\Delta n=\pm1$
	$F_c=0.6$	$\Delta F_c=\pm0.2$	$F_c=\exp(-T/587)$	200—300	
$F+CH_4 \rightarrow HF+CH_3$	$8.0\cdot10^{-11}$	±0.2	$3.0\cdot10^{-10}\exp(-400/T)$	250—450	±200
$HO+CH_3CHF_2 \rightarrow$ products	$3.4\cdot10^{-14}$	±0.2	—	—	—
$HO+CH_2FCF_3 \rightarrow H_2O+CHFCF_3$	$8.4\cdot10^{-15}$	±0.2	$6.6\cdot10^{-13}\exp(-1300/T)$	250—440	±300
$FO+O_3 \rightarrow$ products	no recommended value see Ref.9				
$FO+NO \rightarrow F+NO_2$	$2.6\cdot10^{-11}$	±0.3	—	—	—
$FO+NO_2+M \rightarrow FONO_2+M$	$1.6\cdot10^{-31}\ [O_2]$ (k_0)	±0.7	$1.6\cdot10^{-31}\ (T/300)^{-3.4}[O_2]$	200—300	$\Delta n=\pm1.0$
	$1.6\cdot10^{-31}\ [N_2]$ (k_0)	±0.7	$1.6\cdot10^{-31}\ (T/300)^{-3.4}[N_2]$	200—300	$\Delta n=\pm1.0$
	$2\cdot10^{-11}$ (k_∞)	±0.5	$2\cdot10^{-11}$	200—300	$\Delta n=\pm0.5$
	$F_c=0.5$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/433)$	200—300	—
$FO+FO \rightarrow$ products	$1.5\cdot10^{-11}$	±0.3	—	—	—
$HF+h\nu \rightarrow$ products	see Ref.9				
$FONO_2+h\nu \rightarrow$ products	see Ref.9				
$COF_2+h\nu \rightarrow$ products	see Ref.9				
		ClO_x reactions			
$O+HCl \rightarrow HO+Cl$	$1.4\cdot10^{-16}$	±0.3	$1.0\cdot10^{-11}\exp(-3340/T)$	293—718	±350
$O+HOCl \rightarrow HO+ClO$	no recommended value see Ref.9				
$O+ClO \rightarrow O_2+Cl$	$3.8\cdot10^{-11}$	±0.1	$3.8\cdot10^{-11}$	200—300	±250
$O+OClO \rightarrow O_2+ClO$ / $\rightarrow O+ClOO$	$5\cdot10^{-13}$	±0.5	—	—	—
$O+ClONO_2 \rightarrow$ products	$1.9\cdot10^{-13}$	±0.1	$3.0\cdot10^{-12}\exp(-808/T)$	213—295	±200
$O(^1D)+CF_2Cl_2 \rightarrow$ products	$1.4\cdot10^{-10}$	±0.1	—	—	—
$O(^1D)+CFCl_3 \rightarrow$ products	$2.3\cdot10^{-10}$	±0.1	—	—	—
$O(^1D)+CCl_4 \rightarrow$ products	$3.3\cdot10^{-10}$	±0.1	—	—	—
$Cl+H_2 \rightarrow HCl+H$	$1.6\cdot10^{-16}$	±0.1	$3.7\cdot10^{-11}\exp(-2300/T)$	200—300	±200
$Cl+HO_2 \rightarrow HCl+O_2$	$3.2\cdot10^{-11}$	±0.2	$1.8\cdot10^{-11}\exp(+170/T)$	250—420	±250
$\rightarrow ClO+HO$	$9.1\cdot10^{-12}$	±0.3	$4.1\cdot10^{-11}\exp(-450/T)$	250—420	±250
$Cl+H_2O_2 \rightarrow HCl+HO_2$	$4.3\cdot10^{-13}$	±0.2	$1.1\cdot10^{-11}\exp(-980/T)$	265—424	±500
$Cl+O_2+M \rightarrow ClOO+M$	$1.7\cdot10^{-33}\ [N_2]$	±0.3	—	—	—
$ClOO+M \rightarrow Cl+O_2+M$	$2.5.10^{-13}\ [N_2]$ (k/s^{-1})	±0.5	$1.5.10^{-6}\exp(-3285/T)\ [NH_3]\ s^{-1}$	200—300	±1250
$Cl+O_3 \rightarrow ClO+O_2$	$1.2\cdot10^{-11}$	±0.06	$2.7\cdot10^{-11}\exp(-257/T)$	205—298	±100
$Cl+HONO_2 \rightarrow HCl+NO_3$	$<2.0\cdot10^{-16}$	—	—	—	—
$Cl+NO_3 \rightarrow ClO+NO_2$	$2.6\cdot10^{-11}$	±0.3	$2.6\cdot10^{-11}$	200—300	±400
$Cl+CH_4 \rightarrow HCl+CH_3$	$1.0\cdot10^{-13}$	±0.1	$9.6\cdot10^{-12}\exp(-1350/T)$	200—300	±250
$Cl+C_2H_6 \rightarrow HCl+C_2H_5$	$5.7\cdot10^{-11}$	±0.06	$7.7\cdot10^{-11}\exp(-90/T)$	220—350	±100
$Cl+C_3H_8 \rightarrow HCl+C_3H_7$	$1.5\cdot10^{-10}$	±0.2	$1.3\cdot10^{-10}\exp(+40/T)$	220—600	±200
$Cl+HCHO \rightarrow HCl+HCO$	$7.3\cdot10^{-11}$	±0.06	$8.2\cdot10^{-11}\exp(-34/T)$	200—500	±100
$Cl+CH_3CHO \rightarrow HCl+CH_3CO$	$7.6\cdot10^{-11}$	±0.3	—	—	—
$Cl+CH_3CN \rightarrow$ products	$\leq2\cdot10^{-15}$	—	—	—	—
$Cl+OClO \rightarrow 2ClO$	$5.8\cdot10^{-11}$	±0.1	$3.4\cdot10^{-11}\exp(+160/T)$	298—450	±200
$Cl+ClONO_2 \rightarrow Cl_2+NO_3$	$1.2\cdot10^{-11}$	±0.12	$6.8\cdot10^{-12}\exp(+160/T)$	219—298	±200
$Cl+CH_3Cl \rightarrow HCl+CH_2Cl$	$4.9\cdot10^{-13}$	±0.1	$3.4\cdot10^{-11}\exp(-1260/T)$	233—350	±200
$Cl+CH_3CCl_3 \rightarrow HCl+CH_2CCl_3$	$<4\cdot10^{-16}$	±0.1	—	—	—
$HO+HCl \rightarrow H_2O+Cl$	$8.1\cdot10^{-13}$	±0.1	$2.4\cdot10^{-12}\exp(-330/T)$	200—300	±150
$HO+HOCl \rightarrow H_2O+ClO$	$5.0\cdot10^{-13}$	±0.5	$3.0\cdot10^{-12}\exp(-500/T)$	200—300	±500
$HO+ClO \rightarrow HO_2+Cl$ / $\rightarrow HCl+O_2$	$1.7\cdot10^{-11}$	±0.2	$1.1\cdot10^{-11}\exp(+120/T)$	200—373	±150
$HO+OClO \rightarrow HOCl+O_2$	$7.0\cdot10^{-12}$	±0.3	$4.5\cdot10^{-13}\exp(+800/T)$	290—480	±200
$HO+ClONO_2 \rightarrow$ products	$3.9\cdot10^{-13}$	±0.2	$1.2\cdot10^{-12}\exp(-330/T)$	246—387	±200
$HO+CH_3Cl \rightarrow H_2O+CH_2Cl$	$4.2\cdot10^{-14}$	±0.1	$1.9\cdot10^{-12}\exp(-1120/T)$	247—350	±200
$HO+CH_2FCl \rightarrow H_2O+CHFCl$	$4.4\cdot10^{-14}$	±0.1	$2.6\cdot10^{-12}\exp(-1210/T)$	245—350	±100
$HO+CHF_2Cl \rightarrow H_2O+CF_2Cl$	$4.7\cdot10^{-15}$	±0.1	$1.1\cdot10^{-12}\exp(-1620/T)$	250—360	±100
$HO+CHFCl_2 \rightarrow H_2O+CFCl_2$	$3.0\cdot10^{-14}$	±0.1	$1.1\cdot10^{-12}\exp(-1070/T)$	240—350	±100

Table 2 (cont'd.)

Reaction	k_{298}, $cm^3\ s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3\ s^{-1}$	Temperatures range, K	$\Delta (E/R)$, K
		ClO_x reactions			
$HO+CH_2Cl_2 \rightarrow H_2O+CHCl_2$	$1.4\cdot10^{-13}$	±0.1	$4.4\cdot10^{-12}\exp(-1030/T)$	240—300	±250
$HO+CHCl_3 \rightarrow H_2O+CCl_3$	$1.0\cdot10^{-13}$	±0.1	$3.3\cdot10^{-12}\exp(-1030/T)$	240—300	±100
$HO+CFCl_3 \rightarrow HOCl+CFCl_2$	$<5\cdot10^{-18}$	—	$<1\cdot10^{-12}\exp(-3650/T)$	250—480	—
$HO+CF_2Cl_2 \rightarrow HOCl+CF_2Cl$	$<7\cdot10^{-18}$	—	$<1\cdot10^{-12}\exp(-3540/T)$	250—478	—
$HO+CCl_4 \rightarrow HOCl+CCl_3$	$<4\cdot10^{-16}$	—	$<1\cdot10^{-12}\exp(-2320/T)$	—	—
$HO+C_2HCl_3 \rightarrow$ products	$2.2\cdot10^{-12}$	±0.1	$5.0\cdot10^{-13}\exp(+445/T)$	230—420	±200
$HO+C_2Cl_4 \rightarrow$ products	$1.7\cdot10^{-13}$	±0.1	$9.4\cdot10^{-12}\exp(-1200/T)$	300—420	±200
$HO+CH_3CF_2Cl \rightarrow H_2O+CH_2CF_2Cl$	$3.6\cdot10^{-15}$	±0.2	$1.6\cdot10^{-12}\exp(-1820/T)$	270—380	±300
$HO+CHFClCF_3 \rightarrow H_2O+CFClCF_3$	$1.0\cdot10^{-14}$	±0.2	$6.4\cdot10^{-13}\exp(-1240/T)$	250—380	±300
$HO+CH_2ClCF_2Cl \rightarrow H_2O+CHClCF_2Cl$	$1.5\cdot10^{-14}$	±0.3	$3.0\cdot10^{-12}\exp(-1580/T)$	250—350	±500
$HO+CHCl_2CF_3 \rightarrow H_2O+CCl_2CF_3$	$3.4\cdot10^{-14}$	±0.2	$1.2\cdot10^{-12}\exp(-1060/T)$	245—375	±300
$HO+CH_3CCl_3 \rightarrow H_2O+CH_2CCl_3$	$1.2\cdot10^{-14}$	±0.15	$5.1\cdot10^{-12}\exp(-1800/T)$	250—460	±200
$NO_3+C_2HCl_3 \rightarrow$ products	$2.9\cdot10^{-16}$	±0.3	—	—	—
$NO_3+C_2Cl_4 \rightarrow$ products	$<1\cdot10^{-16}$	—	—	—	—
$ClO+HO_2 \rightarrow HOCl+O_2$	$5.0\cdot10^{-12}$	±0.15	$4.6\cdot10^{-13}\exp(+710/T)$	200—300	±300
$\rightarrow HCl+O_3$	$\leqslant2\cdot10^{-14}$	—	—	—	
$ClO+O_2(^1\Delta_g) \rightarrow$ sym-ClO_3	$<3.0\cdot10^{-15}$	—	—	—	—
$ClO+NO \rightarrow Cl+NO_2$	$1.7\cdot10^{-11}$	±0.1	$6.2\cdot10^{-12}\exp(+294/T)$	202—415	±100
$ClO+NO_2+M \rightarrow ClONO_2+M$	$1.7\cdot10^{-31}$ [O_2] (k_0)	±0.1	$1.7\cdot10^{-31}\ (T/300)^{-3.4}$[$O_2$]	200—300	$\Delta n=\pm1.0$
	$1.7\cdot10^{-31}$ [N_2] (k_0)	±0.1	$1.7\cdot10^{-31}\ (T/300)^{-3.4}$[$N_2$]	200—300	$\Delta n=\pm1.0$
	$2\cdot10^{-11}$ (k_∞)	±0.3	$2\cdot10^{-11}$	200—300	$\Delta n=\pm0.5$
	$F_c=0.5$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/430)$	—	—
$ClO+NO_3 \rightarrow ClOO+NO_2$ / $\rightarrow OClO+NO_2$	$4.0\cdot10^{-13}$	±0.3	—	—	—
$ClO+HCHO \rightarrow$ products	$<10^{-15}$	—	—	—	—
$ClO+ClO \rightarrow ClOO+Cl$	$3.4\cdot10^{-15}$	±0.2	—	—	—
$\rightarrow OClO+Cl$	$1.7\cdot10^{-15}$	±0.2	—	—	—
$\rightarrow Cl_2+O_2$	$4.9\cdot10^{-15}$	±0.2	—	—	—
$ClO+ClO+M \rightarrow Cl_2O_2+M$	$4.0\cdot10^{-32}$ [N_2] (k_0)	±0.2	$4.0\cdot10^{-32}\ (T/300)^{-2.0}$[$N_2$]	200—300	$\Delta n=\pm1.0$
$Cl_2O_2+M \rightarrow ClO+ClO+M$	$6.1\cdot10^{-18}$ [N_2] (k_0/s^{-1})	±0.5	$3.1\cdot10^{-5}\ (T/300)^{-3}\exp(-8720/T)$ [N_2] s^{-1}	230—300	±500
$OClO+NO \rightarrow ClO+NO_2$	$3.4\cdot10^{-13}$	±0.3	—	—	—
$ClONO_2+H_2O \rightarrow HOCl+HONO_2$	$<5.0\cdot10^{-21}$	—	—	—	—
$ClONO_2+HCl \rightarrow Cl_2+HONO_2$	$<2.0\cdot10^{-20}$	—	—	—	—
$CF_3+O_2+M \rightarrow CF_3O_2+M$	$1.9\cdot10^{-29}$ [N_2] (k_0)	±0.2	$1.9\cdot10^{-29}\ (T/300)^{-4.7}$[$N_2$]	200—400	$\Delta n=\pm1$
	$1\cdot10^{-11}$ (k_∞)	±0.2	$1\cdot10^{-11}$	200—400	—
	$F_c=0.4$—0.5	—	—	—	—
$CFCl_2+O_2+M \rightarrow CFCl_2O_2+M$	$5\cdot10^{-30}$ [N_2] (k_0)	±0.4	$5\cdot10^{-30}\ (T/300)^{-4}$[$N_2$]	200—300	$\Delta n=\pm2$
	$6\cdot10^{-12}$ (k_∞)	±0.5	$6\cdot10^{-12}$	200—300	—
	$F_c=0.6$	—	—	—	—
$CCl_3+O_2+M \rightarrow CCl_3O_2+M$	$1.5\cdot10^{-30}$ [N_2] (k_0)	±0.5	$1.5\cdot10^{-30}\ (T/300)^{-4}$[$N_2$]	200—300	$\Delta n=\pm2$
	$5\cdot10^{-12}$ (k_∞)	±0.5	$5\cdot10^{-12}$	200—300	—
	$F_c=0.25$				
$CCl_3O \rightarrow CCl_2O+Cl$	$>1.10^5\ s^{-1}$ (233 K, 7.5 mmHg)	—	—	—	—
$CCl_2FO \rightarrow CClFO+Cl$	$>3.10^4\ s^{-1}$ (253 K, 6.7 mmHg)	—	—	—	—
$CF_3O_2+NO \rightarrow CF_3O+NO_2$	$1.6\cdot10^{-11}$	±0.2	$1.6\cdot10^{-11}\ (T/300)^{-1.2}$	230—430	—
$CF_2ClO_2+NO \rightarrow CF_2ClO+NO_2$	$1.6\cdot10^{-11}$	±0.3	$1.6\cdot10^{-11}\ (T/300)^{-1.5}$	230—430	—
$CFCl_2O_2+NO \rightarrow CFCl_2O+NO_2$	$1.5\cdot10^{-11}$	±0.2	$1.5\cdot10^{-11}\ (T/300)^{-1.3}$	230—430	—
$CCl_3O_2+NO \rightarrow CCl_3O+NO_2$	$1.8\cdot10^{-11}$	±0.2	$1.8\cdot10^{-11}\ (T/300)^{-1.0}$	230—430	—
$CF_3O_2+NO_2+M \rightarrow CF_3O_2NO_2+M$	$2.7\cdot10^{-29}$ [N_2] (k_0)	±0.3	$2.7\cdot10^{-29}\ (T/300)^{-5}$[$N_2$]	200—300	$\Delta n=\pm2$
	$9\cdot10^{-12}$ (k_∞)	±0.5	$9\cdot10^{-12}\ (T/300)^{-0.7}$	200—300	$\Delta n=\pm1$
	$F_c=0.49$		$F_c=\exp(-T/416)$	—	—
$CF_2ClO_2+NO_2+M \rightarrow CF_2ClO_2NO_2+M$	$4.0\cdot10^{-29}$ [N_2] (k_0)	±0.4	$4.0\cdot10^{-29}\ (T/300)^{-5}$[$N_2$]	200—300	$\Delta n=\pm2$
	$1.0\cdot10^{-11}$ (k_∞)	±0.5	$1.0\cdot10^{-11}\ (T/300)^{-0.7}$	200—300	$\Delta n=\pm1$
	$F_c=0.45$	—	$F_c=\exp(-T/373)$	—	—
$CF_2ClO_2NO_2+M \rightarrow CF_2ClO_2+NO_2+M$	$1.5.10^{-17}$ [N_2] (k_0/s^{-1})	±0.3	$5.6.10^{-4}\exp(-9310/T)$ [N_2] s^{-1}	260—290	±1000
	$4.9.10^{-2}$ (k_∞/s^{-1})	±0.3	$1.0.10^{16}\exp(-11880/T)\ s^{-1}$	260—290	±1000
	$F_c=0.4$	—	—	—	—
$CFCl_2O_2+NO_2+M \rightarrow CFCl_2O_2NO_2+M$	$5.5\cdot10^{-29}$ [N_2] (k_0)	±0.3	$5.5\cdot10^{-29}\ (T/300)^{-5}$[$N_2$]	200—300	$\Delta n=\pm1$
	$8.3\cdot10^{-12}$ (k_∞)	±0.3	$8.3\cdot10^{-12}\ (T/300)^{-0.7}$	200—300	$\Delta n=\pm1$
	$F_c=0.42$		$F_c=\exp(-T/342)$	—	—
$CFCl_2O_2NO_2+M \rightarrow CFCl_2O_2+NO_2+M$	$1.2.10^{-18}$ [N_2] (k_0/s^{-1})	±0.3	$3.10^{-3}\exp(-10570/T)$ [N_2] s^{-1}	270—290	±1000
	$7.3.10^{-2}$ (k_∞/s^{-1})	±0.3	$2.1.10^{16}\exp(-11980/T)\ s^{-1}$	270—290	±1000
	$F_c=0.4$		$F_c=\exp(-T/342)$	—	—
$CCl_3O_2+NO_2+M \rightarrow CCl_3O_2NO_2+M$	$9.2\cdot10^{-29}$ [N_2] (k_0)	±0.3	$9.2\cdot10^{-29}\ (T/300)^{-6}$[$N_2$]	200—300	$\Delta n=\pm2$
	$1.5\cdot10^{-11}$ (k_∞)	±0.3	$1.5\cdot10^{-11}\ (T/300)^{-0.3}$	200—300	$\Delta n=\pm1$
	$F_c=0.32$		$F_c=\exp(-T/260)$	—	—
$CCl_3O_2NO_2+M \rightarrow CCl_3O_2+NO_2+M$	$1.5.10^{-17}$ [N_2] (k_0/s^{-1})	±0.3	$5.6\cdot10^{-4}\exp(-9310/T)$ [N_2]	260—300	±1000
	$1.6.10^{-1}$ (k_∞/s^{-1})	±0.3	$9.1.10^{14}\exp(-10820/T)\ s^{-1}$	260—300	±1000
	$F_c=0.20$				
$CH_2ClO_2NO_2+M \rightarrow CH_2ClO_2+NO_2+M$	см. [9]				

Table 2 (cont'd.)

Reaction	k_{298}, $cm^3\ s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3\ s^{-1}$	Temperatures range, K	$\Delta(E/R)$, K
		ClO_x reactions			
$O_3+C_2HCl_3\rightarrow$products	$<5\cdot10^{-20}$	—	—	—	—
$O_3+C_2Cl_4\rightarrow$products	$<10^{-21}$	—	—	—	—
$HOCl+h\nu\rightarrow$products	see Ref.9				
$OClO+h\nu\rightarrow$products	see Ref.9				
$Cl_2O_2+h\nu\rightarrow$products	see Ref.9				
$ClONO_2+h\nu\rightarrow$products	see Ref.9				
$COFCl+h\nu\rightarrow$products	see Ref.9				
$COCl_2+h\nu\rightarrow$products	see Ref.9				
$CF_2Cl_2+h\nu\rightarrow$products	see Ref.9				
$CFCl_3+h\nu\rightarrow$products	see Ref.9				
$CCl_4+h\nu\rightarrow$products					
		BrO_x reactions			
$O+HBr\rightarrow HO+Br$	$3.7\cdot10^{-14}$	±0.12	$6.6\cdot10^{-12}\exp(-1540/T)$	220—455	±200
$O+Br_2\rightarrow BrO+Br$	$1.4\cdot10^{-11}$	±0.2	—	—	—
$O+BrO\rightarrow O_2+Br$	$3\cdot10^{-11}$	±0.5	—	—	—
$Br+HO_2\rightarrow HBr+O_2$	$2.0\cdot10^{-12}$	±0.3	$1.4\cdot10^{-11}\exp(-590/T)$	260—390	±200
$Br+H_2O_2\rightarrow HBr+HO_2$ } $\rightarrow HOBr+HO$ }	$<5\cdot10^{-16}$	—	—	—	—
$Br+O_3\rightarrow BrO+O_2$	$1.2\cdot10^{-12}$	±0.1	$1.7\cdot10^{-11}\exp(-800/T)$	220—360	±200
$Br+HCHO\rightarrow HBr+HCO$	$1.0\cdot10^{-12}$	±0.15	$1.7\cdot10^{-11}\exp(-800/T)$	223—480	±250
$Br+CH_3CHO\rightarrow HBr+CH_3CO$	$3.6\cdot10^{-12}$	±0.2			
$Br+OClO\rightarrow BrO+ClO$	$3.4\cdot10^{-13}$	±0.3	$2.6\cdot10^{-11}\exp(-1300/T)$	200—450	±300
$HO+HBr\rightarrow H_2O+Br$	$1.1\cdot10^{-11}$	±0.1	$1.1\cdot10^{-11}$	249—416	±250
$HO+Br_2\rightarrow HOBr+Br$	$4.5\cdot10^{-11}$	±0.15	$1.2\cdot10^{-11}\exp(+400/T)$	260—360	±400
$HO+CH_3Br\rightarrow H_2O+CH_2Br$	$3.8\cdot10^{-14}$	±0.1	$7.6\cdot10^{-13}\exp(-890/T)$	244—350	±200
$BrO+HO_2\rightarrow HOBr+O_2$ } $\rightarrow HBr+O_3$ }	$5\cdot10^{-12}$	±0.5	—	—	—
$BrO+O_3\rightarrow Br+2O_2$	$<5\cdot10^{-15}$	—	—	—	—
$BrO+NO\rightarrow Br+NO_2$	$2.1\cdot10^{-11}$	±0.1	$8.7\cdot10^{-12}\exp(+260/T)$	224—425	±100
$BrO+NO_2+M\rightarrow BrONO_2+M$	$5.0\cdot10^{-31}[O_2]$ (k_0)	±0.3	$5.0\cdot10^{-31}(T/300)^{-3.0}[O_2]$	200—300	$\Delta n=\pm1$
	$5.0\cdot10^{-31}[N_2]$ (k_0)	±0.3	$5.0\cdot10^{-31}(T/300)^{-3.0}[N_2]$	200—300	$\Delta n=\pm1$
	$2\cdot10^{-11}$ (k_∞)	±0.3	$2\cdot10^{-11}$	200—300	$\Delta n=\pm0.5$
	$F_c=0.4$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/327)$	200—300	—
$BrO+ClO\rightarrow Br+OClO$	$6.9\cdot10^{-12}$	±0.1	$1.9\cdot10^{-12}\exp(+390/T)$	200—400	±400
$\rightarrow Br+ClOO$ } $\rightarrow BrCl+O_2$ }	$6.4\cdot10^{-12}$	±0.1	$3.9\cdot10^{-12}\exp(+140/T)$	200—400	±200
$BrO+BrO\rightarrow 2Br+O_2$	$2.2\cdot10^{-12}$	±0.1 }	$1.1\cdot10^{-12}\exp(+255/T)$	223—398	±300
$\rightarrow Br_2+O_2$	$4.5\cdot10^{-13}$	±0.2 }			
$HOBr+h\nu\rightarrow$products	см. [9]				
$BrO+h\nu\rightarrow$products	см. [9]				
$BrONO_2+h\nu\rightarrow$products	см. [9]				
		IO_x reactions			
$O+I_2\rightarrow IO+I$	$1.4\cdot10^{-10}$	±0.3	$1.4\cdot10^{-10}$	200—400	±250
$O+IO\rightarrow O_2+I$	$5\cdot10^{-11}$	±0.5	—	—	—
$I+HO_2\rightarrow HI+O_2$	no recommended value see Ref.9				
$I+O_3\rightarrow IO+O_2$	$9.5\cdot10^{-13}$	±0.2			
$I+NO+M\rightarrow INO+M$	$1.8\cdot10^{-32}[O_2]$ (k_0)	±0.2	$1.8\cdot10^{-32}(T/300)^{-1.0}[O_2]$	200—300	$\Delta n=\pm0.5$
	$1.8\cdot10^{-32}[N_2]$ (k_0)	±0.1	$1.8\cdot10^{-32}(T/300)^{-1.0}[N_2]$	200—300	$\Delta n=\pm0.5$
	$1.7\cdot10^{-11}$ (k_∞)	±0.3	$1.7\cdot10^{-11}$	200—300	$\Delta n=\pm0.5$
	$F_c=0.75$	$\Delta F_c=\pm0.15$	$F_c=\exp(-T/1043)$		
$I+NO_2+M\rightarrow INO_2+M$	$2.9\cdot10^{-31}[O_2]$ (k_0)	±0.3	$2.9\cdot10^{-31}(T/300)^{-1.0}[O_2]$	200—300	$\Delta n=\pm0.5$
	$2.9\cdot10^{-31}[N_2]$ (k_0)	±0.3	$2.9\cdot10^{-31}(T/300)^{-1.0}[N_2]$	200—300	$\Delta n=\pm0.5$
	$6.6\cdot10^{-11}$ (k_∞)	±0.3	$6.6\cdot10^{-11}$	200—300	$\Delta n=\pm0.5$
	$F_c=0.63$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/650)$	—	—
$HO+HI\rightarrow H_2O+I$	$1.3\cdot10^{-11}$	±0.5	—	—	—
$HO+I_2\rightarrow HOI+I$	$1.8\cdot10^{-10}$	±0.3	—	—	—
$IO+HO_2\rightarrow$products	no recommended value				
$IO+IO\rightarrow$products	$5.2\cdot10^{-11}$ (1 atm)	±0.5	$1.7\cdot10^{-12}\exp(+1020/T)$ (1 atm)	250—373	±200
$IO+NO\rightarrow I+NO_2$	$1.7\cdot10^{-11}$	±0.3	—	—	—
$IO+NO_2+M\rightarrow IONO_2+M$	$3.4\cdot10^{-31}[O_2]$ (k_0)	±0.5	$3.4\cdot10^{-31}(T/300)^{-3.0}[O_2]$	200—400	$\Delta n=\pm1$
	$3.4\cdot10^{-31}[N_2]$ (k_0)	±0.5	$3.4\cdot10^{-31}(T/300)^{3.0}[N_2]$	200—400	$\Delta n=\pm1$
	$1.6\cdot10^{-11}$ (k_∞)	±0.5	$1.6\cdot10^{-11}$	200—400	$\Delta n=\pm0.5$
	$F_c=0.4$	$\Delta F_c=\pm0.1$	$F_c=\exp(-T/327)$	—	—
$IO+CH_3SCH_3\rightarrow$products	no recommended value				
$INO+INO\rightarrow I_2+2NO$	$1.3\cdot10^{-14}$	±0.4	$8.4\cdot10^{-11}\exp(-2620/T)$	298—450	±600

Table 2 (cont'd.)

Reaction	k_{298}, $cm^3 s^{-1}$	$\Delta \lg k_{298}$	Temperature dependence of K, $cm^3 s^{-1}$	Temperatures range, K	$\Delta (E/R)$, K
			IO_x reactions		
$INO_2 + NIO_2 \rightarrow I_2 + 2NO_2$	$4.7 \cdot 10^{-15}$	± 0.5	$2.9 \cdot 10^{-11} \exp(-2600/T)$	298—400	± 1000
$HOI + h\nu \rightarrow$ products	see Ref.9				
$IO + h\nu \rightarrow$ products	see Ref.9				
$INO + h\nu \rightarrow$ products	see Ref.9				
$INO_2 + h\nu \rightarrow$ products	see Ref.9				
$IONO_2 + h\nu \rightarrow$ products	see Ref.9				

3. Photochemical reactions

In CODATA/IUPAC reviews, tables of data begin with a list of the primary photochemical transitions at wavelengths not less than 170 nm. Also presented are the corresponding enthalpy changes at 0 K when this is possible, otherwise the values of 298 K are given. Also listed are the threshold wavelengths corresponding to these enthalpy changes. Next, the existing experimental data for the absorption cross-sections and quantum yields are compiled. These data are accompanied by commentaries. After that, the recommended absorption cross-sections and quantum yields for different wavelengths are listed wherever possible at 5 nm intervals. In many cases diagrams illustrating the dependence of the absorption cross-sections and quantum yields on the wavelength are shown as well. The choice of the recommended values is justified in the commentaries and certain other questions are considered.

4. Absorption cross-sections

In the CODATA/IUPAC compilations of data, these quantities are listed under the heading "absorption cross-sections per molecule to base e". They were determined in accordance with the equation

$$I/I_0 = \exp(-\sigma N l),$$
$$\sigma = (1/(Nl)) \cdot \ln(I_0/I),$$

where I_0 and I are the intensities of the incident and transmitted light, σ is the absorption cross-section (cm^2), N the number of particles of the absorbing substance (cm^{-3}) and l the distance traversed by the beam (cm). Other definitions and units of the measurement are also used. The closely related "absorption coefficient" and "extinction coefficients" are frequently quoted, but their definitions should not be confused. It is always necessary to draw attention to the units of the measurement of concentration, the traversed distance, and also the type of logarithm used in the definition (natural or decadic).

5. Determination of errors

The estimates of the absolute errors of the recommended values of k at 298 K and of the quantities E/R in the temperature range indicated are listed in the CODATA/IUPAC tables under the heading "reliability". These limits of errors are also given below in Table 2. The errors of the recommended rate constants at 298 K are expressed by the term

$$\Delta \lg k = D; \quad \lg k = C \pm D.$$

This is equivalent to the determination of k to within a multiplier F, where $D = \lg F$. The accuracy of the recommended values of E/R is expressed by the term $\Delta(E/R)$, where $\Delta(E/R) = G$ and G is defined by the equation $E/R = H \pm G$.

The absolute errors in k and E/R were determined by the Expert Panel. Experience has shown that, for the reactions of atoms and free radicals in the gas phase, the accuracy (reproducibility) of the measurements is usually good. Thus, for a separate investigation of a specified reaction by this method, the standard deviation (or even the 90% confidence interval) is, as stated in the literature, not more than $\pm 10\%$. Unfortunately, when data obtained by different groups of investigators using different methods for the same reaction are compared, it is frequently found that the rate constants differ by a factor of 2 or even more. This means that one or several investigations involve large systematic errors, which are difficult to detect. This is not surprising since, in contrast to molecular reactions, it is not always possible to investigate the reactions of atoms and radicals in isolation and hence experimental difficulties frequently arise.

The critical evaluations of errors in the CODATA/IUPAC selections are based mainly on the state of our knowledge for a particular reaction, which depends on the number of studies carried out and on the number of methods employed. Overall, the limits of error have been expanded. Thus in the case of a single study by one method not confirmed by independent investigations, limits of at least double errors indicated are adopted.

V. Table of reactions and recommended kinetic quantities

A complete list of chemical reactions and recommended kinetic parameters from the latest IUPAC survey is presented in Table 2. Unfortunately, it was not possible to present photochemical data in a compact form and we refer the reader to the complete CODATA/IUPAC publications[9].

* * *

At the time of the publication of the CODATA (Supplement 11) [39] and NASA (No. 7) [40] surveys, it was believed that the principal features of stratospheric gas-phase chemistry, including the constants of the key reactions, had been thoroughly established. At the present time additional requirements as regards the heterogeneous chemistry of polar stratospheric clouds, which may help to explain the appearance of Antarctic "ozone holes", must be added to this statement. A kinetic data bank for the chemistry of polar stratospheric clouds is being rapidly created at the present time, which should be reflected in extended surveys by both the NASA Group and the IUPAC Subcommittee for the Estimation of Gas-Kinetic Data for Atmospheric Chemistry. The second of these groups has begun to formulate a survey of kinetic data for reactions, mainly of organic species, which play a key role in the chemistry of the troposphere.

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Problems of the distribution of the global aerosol

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ABSTRACT. In view of the short residence time of the aerosol in the atmosphere, knowledge of its distribution in space is essential for the understanding of many processes associated with this distribution, for example, the formation of clouds and hence of the entire cloud cover over the Earth's sphere. This review considers both the distribution of aerosol particles with respect to size (from the standpoint of chemical and physical characteristics) and the distribution of aerosols in space in a broad sense of this term.

The bibliography includes 55 references.

Contents

I. Introduction 959
II. Distribution of the aerosol in space and time 959
III. Distribution of aerosol particles with respect to size 960
IV. Dependence of the properties of the aerosol on the particle size 963
V. Horizontal or geographical distribution of the aerosol 967
VI. Vertical distribution of the aerosol 969
VII. Conclusion 971

I. Introduction

Apart from the main gases (nitrogen and oxygen), the atmosphere contains small admixtures of other substances. Investigators working in the following fields of meteorology and atmospheric chemistry are concerned with the study of these admixtures: (1) the physics and chemistry of clouds (water); (2) the chemistry of gaseous impurities; (3) the physics and chemistry of aerosols.

Compared with the bulk of the main gases contained in one cubic metre of dry air, which is ~1300 g (this quantity depends on temperature), the overall content of water in all three states of aggregation is less than 10 g, that of gaseous admixtures (excluding water) is up to 0.5 g, and that of aerosol particles is up to 50 mg. Thus the mass concentration of the aerosol does not exceed that of minor gaseous admixtures. For this reason many scientists and unfortunately society in general underestimate the importance of aerosols in view of the low ratio of the mass concentration of the aerosol to the mass concentration of the gaseous admixtures.

Nevertheless, aerosols play a key role in the atmosphere. For example, certain aerosol particles serve as condensation nuclei for water vapour in clouds, so that the turnover of water in the absence of these particles would change significantly and hence the climate of the Earth would also change.

For example, half of the total amount of the aerosol is formed as a result of the gas–particle transformation (including both homogeneous and heterogeneous condensation) and this process is therefore an important route leading to the removal of many gaseous species from the atmosphere.

Aerosol particles consist of a large set of chemical substances (organic and inorganic) minerals, and particles of biogenic origin. The influence of aerosol on man and the environment is due to the presence of these compounds, whose concentrations are sometimes very low (of the order of a nanogram per cubic metre as in the case of certain specific organic compounds or pollen particles).

The question arises why aerosols play such an important role in the atmosphere. Firstly, they influence the field of the Earth's electromagnetic radiation as a whole, since they absorb and scatter a large proportion of the incident solar radiation; secondly, they ensure the presence, directly in the gas phase, of a large surface area for the occurrence of chemical reactions of various gaseous substances; thirdly, they influence the turnover of atmospheric water, since they serve as condensation nuclei in clouds; fourthly, they provide a surface on which natural radioactive nuclides are adsorbed; fifthly, they influence the chemical and radiation (albedo) properties of the surface of the planet as a result of the dry and wet precipitation on its surface; sixthly, they alter the electric field of the atmosphere, since aerosol particles can be charged; finally, they promote the spread of plants and diseases.

It is difficult to estimate the influence of the aerosol on the state of the atmosphere, because in a geochemical sense the aerosol particles have a very short lifetime. Furthermore, there are additional meteorological characteristics (horizontal, vertical, and time distributions of the aerosol) and there exists a distribution of the particles with respect to size (the number, surface, and mass concentrations, the chemical properties, and the refractive index are different for particles of different size) which hinders in its turn the determination of their influence. It is also noteworthy that, among all the components of the atmosphere, the suspended substances are unique as regards the complexity of their chemical composition.[1]

To facilitate the description and study of such a complex system and to investigate its influence on the environment, scientists have introduced various parameters such as the electrical conductivity of air, the mass concentration of the aerosol, the extinction coefficient, etc. The present state of knowledge about the entire wide variety of the parameters of the atmospheric aerosol will be described in this review.

II. Distribution of the aerosol in space and time

The term "distribution" has many meanings even if it is understood in a fairly narrow sense. In the physics and chemistry of aerosols, this term usually means the number or volume distribution of particles with respect to size and more rarely the spatial or geographical distribution.

Henceforth we shall discuss the fact that aerosol particles have a polydisperse distribution with respect to size associated with different mechanisms of their formation. After their appearance, aerosol particles undergo a change in their chemical and disperse compositions.

Meteorological processes mix the aerosol in the vertical and horizontal directions. This process involves all the particles regardless of their size and chemical composition.

Other processes act only on specific particles depending on their size and chemical properties. Gravitational influences on the largest particles regardless of their composition forces them to move towards the surface of the Earth. Brownian motion is responsible for the process called "thermal diffusion", which is also independent of the chemical nature of the particles. As a result of thermal diffusion, small particles, having the maximum mobility, collide with other particles and thus coagulate. Cloud drops are formed on aerosol particles with a specific chemical composition, coagulate into larger drops, and are finally precipitated as rain or evaporate once more.[2]

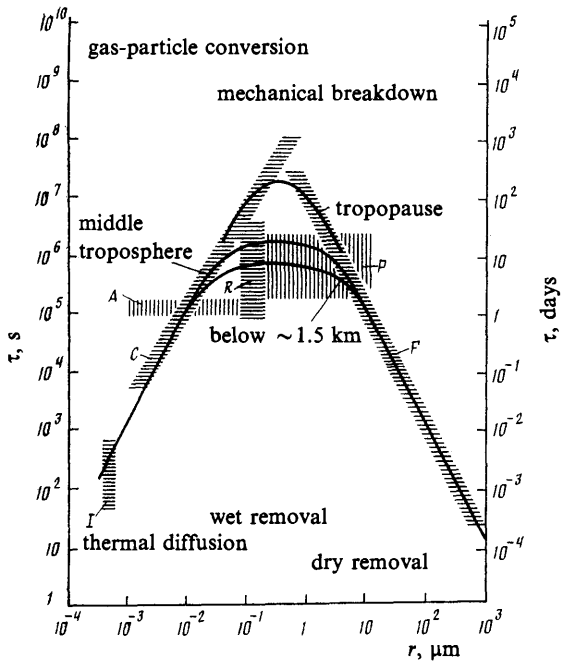


Figure 1. Dependence of the lifetime (τ) of aerosol particles on their radius.[3] The calculation was performed taking into account different independent data: *A*—distribution of Aitken particles in space; *C*—diffusion of the aerosol in dynamic equilibrium; *R*—radioactivity data; *P*—results of studies of the atmospheric water cycle; *F*—sedimentation data.[4]

All these processes limit the residence time of the aerosol particles in the atmosphere, altering thereby their size distribution. The principal result of the influence of these processes is the removal from the atmosphere of the smallest and largest particles and hence the conversion of the polydisperse aerosol into a monodisperse aerosol. This process is called "ageing". Fig. 1 illustrates the dependence of the lifetime of the aerosol particles in the atmosphere on their radius.[3] Small and large particles have shorter lifetimes and only particles with radii in the range 0.1–1 μm exist longer in the suspended state. This time might be longer in the absence of interactions of the aerosol with clouds, a situation which occurs in the upper troposphere and in the stratosphere.

In this connection, it must be emphasised that the term "lifetime" used in this article is not identical with the chemical or geochemical concept of the lifetime of a chemical compound, since the compounds contained in aerosols can continue to be present in the atmosphere after the coagulation of the aerosol particles. There is also another possibility: chemicals can pass from one set of particles to another, differing in size and behaving quite differently in the atmosphere. Yet another remark may be made—the significance of the lifetime in a reactor such as the atmosphere is that of the period during which the concentration of the compound diminishes by a factor *e*. Fig. 1 shows that the lifetime is a maximum for particles with radii in the range 0.1–1 μm and amounts to ~8 days (for the lower troposphere).

It has been suggested[5] that there is an inverse relation between fluctuations in time and space and the lifetime. Substances with a long lifetime are distributed more uniformly. Atmospheric oxygen, for which only rare, episodic measurements of its concentration have been recommended, may serve as a good example.[6] The lifetime of sulphur dioxide is short and SO_2 therefore exhibits pronounced fluctuations in time and space. An equation describing these fluctuations was obtained subsequently[7] using a simple model:

$$V^2 = \frac{1 - \exp(-2T_{max}/T)}{2[1 - \exp(-T_{max}/T)]^2} \frac{T_{max}}{T} - 1,$$

where V is the relative standard deviation (variance), T the lifetime in arbitrary units of time, and T_{max} the "maximum" time (in arbitrary units) during which the admixture exists as an individual compound (T_{max} varies from 10 h to 30 days).

It must be emphasised that there are contradictory attitudes to this statistical approach.[8] Nevertheless, there is qualitative agreement concerning the inverse proportionality between the lifetime and the fluctuation and also about the fact that substances with a lifetime amounting to days should have a standard deviation in their distribution in time and space equal to ~2, while for substances with a shorter lifetime the standard deviation should be much greater.

The dependence of the lifetime of aerosol particles on their size influences the behaviour of the aerosol as a function of time and its distribution in space.

In evaluating the data presented in this review, one must take into account the possible long-time changes in the characteristics of the aerosol under the influence of natural and anthropogenic factors. To some extent, such changes have been summarised in the author's previous communication.[3] Thus any aerosol distribution can reflect the situation only at the time to which it refers.

III. Distribution of aerosol particles with respect to size

Among all the types of distribution of the atmospheric aerosol with respect to size, the most important is the distribution of the number concentration of the particles with respect to diameter,

Table 1. Parameters of the number distribution of the aerosol and its integral characteristics for the size ranges indicated and for the aerosol as a whole.

Type of aerosol	Size ranges	Subrange $10^{-7} < r < 10^{-5}$ cm			Subrange $10^{-7} < r < 10^{-4}$ cm			Subrange $r > 10^{-4}$ cm			Total range $r > 10^{-1}$ cm		
	type of particles according to Junge	Aitken			large			giant			sum		
	fraction according to Whitby	nucleation			accumulation			coarsely disperse					
	aerosol parameters i	n_i	R_i	$\lg\sigma_i$	n_i	R_i	$\lg\sigma_i$	n_i	R_i	$\lg\sigma_i$			
	sum for subranges I'	N'	S'	V'	N'	S'	V'	N'	S'	V'	N	S	V
Polar	$i=1$	$2.17\cdot10^{1}$	$6.89\cdot10^{-6}$	0.245							$2.17\cdot10^{1}$	$2.45\cdot10^{-8}$	$1.24\cdot10^{-13}$
	$i=2$				$1.86\cdot10^{-1}$	$3.75\cdot10^{-5}$	0.300				$1.86\cdot10^{-1}$	$8.54\cdot10^{-9}$	$3.52\cdot10^{-13}$
	$i=3$							$3.04\cdot10^{-4}$	$4.29\cdot10^{-4}$	0.291	$3.04\cdot10^{-4}$	$1.73\cdot10^{-9}$	$7.56\cdot10^{-13}$
	I'	$1.63\cdot10^{1}$	$8.01\cdot10^{-9}$	$1.94\cdot10^{-14}$	$5.83\cdot10^{0}$	$2.13\cdot10^{-8}$	$1.98\cdot10^{-13}$	$1.53\cdot10^{-2}$	$5.92\cdot10^{-9}$	$1.02\cdot10^{-12}$	$2.19\cdot10^{1}$	$3.47\cdot10^{-8}$	$1.23\cdot10^{-12}$
Background tropospheric	$i=1$	$1.29\cdot10^{2}$	$3.60\cdot10^{-7}$	0.645							$1.04\cdot10^{2}$	$1.73\cdot10^{-8}$	$5.12\cdot10^{-13}$
	$i=2$				$5.97\cdot10^{1}$	$1.27\cdot10^{-5}$	0.253				$5.97\cdot10^{1}$	$2.39\cdot10^{-7}$	$2.36\cdot10^{-12}$
	$i=3$				$6.35\cdot10^{-1}$	$2.59\cdot10^{-5}$	0.425				$6.35\cdot10^{-1}$	$3.63\cdot10^{-8}$	$3.44\cdot10^{-12}$
	I'	$1.03\cdot10^{2}$	$1.84\cdot10^{-8}$	$4.55\cdot10^{-14}$	$4.19\cdot10^{1}$	$2.44\cdot10^{-7}$	$2.56\cdot10^{-12}$	$7.71\cdot10^{-2}$	$3.20\cdot10^{-8}$	$3.71\cdot10^{-12}$	$1.65\cdot10^{2}$	$2.92\cdot10^{-7}$	$6.31\cdot10^{-12}$
Marine	$i=1$	$1.33\cdot10^{2}$	$3.90\cdot10^{-7}$	0.657							$1.09\cdot10^{2}$	$2.47\cdot10^{-8}$	$9.66\cdot10^{-13}$
	$i=2$				$6.66\cdot10^{1}$	$1.33\cdot10^{-5}$	0.210				$6.66\cdot10^{1}$	$2.36\cdot10^{-7}$	$1.88\cdot10^{-12}$
	$i=3$				$3.06\cdot10^{0}$	$2.90\cdot10^{-5}$	0.396				$3.06\cdot10^{0}$	$1.71\cdot10^{-7}$	$1.32\cdot10^{-11}$
	I'	$1.25\cdot10^{2}$	$1.90\cdot10^{-8}$	$4.76\cdot10^{-14}$	$5.26\cdot10^{1}$	$2.90\cdot10^{-7}$	$3.12\cdot10^{-12}$	$2.84\cdot10^{-1}$	$1.22\cdot10^{-7}$	$1.29\cdot10^{-11}$	$1.78\cdot10^{2}$	$4.32\cdot10^{-7}$	$1.60\cdot10^{-11}$
Background continental	$i=1$	$9.97\cdot10^{2}$	$1.00\cdot10^{-7}$	0.328							$5.05\cdot10^{2}$	$3.67\cdot10^{-10}$	$5.37\cdot10^{-17}$
	$i=2$	$8.42\cdot10^{2}$	$2.18\cdot10^{-6}$	0.505							$8.39\cdot10^{2}$	$7.51\cdot10^{-7}$	$1.60\cdot10^{-11}$
	$i=3$							$7.10\cdot10^{-4}$	$6.24\cdot10^{-4}$	0.277	$7.10\cdot10^{-4}$	$7.83\cdot10^{-9}$	$4.51,10^{-12}$
	I'	$1.26\cdot10^{3}$	$1.19\cdot10^{-7}$	$2.42\cdot10^{-13}$	$8.11\cdot10^{1}$	$5.13\cdot10^{-7}$	$6.59\cdot10^{-12}$	$4.37\cdot10^{-1}$	$1.35\cdot10^{-7}$	$1.39\cdot10^{-11}$	$1.34\cdot10^{3}$	$7.60\cdot10^{-7}$	$2.05\cdot10^{-11}$
Desert sandstorm	$i=1$	$7.26\cdot10^{2}$	$1.00\cdot10^{-7}$	0.247							$3.69\cdot10^{2}$	$1.53\cdot10^{-10}$	$1.25\cdot10^{-17}$
	$i=2$	$1.14\cdot10^{3}$	$1.88\cdot10^{-6}$	0.770							$1.08\cdot10^{3}$	$2.72\cdot10^{-5}$	$3.51\cdot10^{-8}$
	$i=3$							$1.78\cdot10^{-1}$	$1.08\cdot10^{-3}$	0.438	$1.78\cdot10^{-1}$	$2.00\cdot10^{-5}$	$8.49\cdot10^{-8}$
	I'	$1.26\cdot10^{3}$	$1.28\cdot10^{-7}$	$2.74\cdot10^{-13}$	$1.85\cdot10^{2}$	$2.52\cdot10^{-6}$	$4.68\cdot10^{-11}$	$1.47\cdot10^{1}$	$4.43\cdot10^{-5}$	$1.35\cdot10^{-7}$	$1.45\cdot10^{3}$	$4.72\cdot10^{-5}$	$1.20\cdot10^{-7}$
Agricultural region	$i=1$	$6.65\cdot10^{3}$	$7.39\cdot10^{-7}$	0.225							$6.65\cdot10^{3}$	$7.81\cdot10^{-8}$	$3.76\cdot10^{-14}$
	$i=2$	$1.47\cdot10^{2}$	$2.69\cdot10^{-6}$	0.557							$1.46\cdot10^{2}$	$3.59\cdot10^{-7}$	$1.95\cdot10^{-11}$
	$i=3$	$1.99\cdot10^{3}$	$4.19\cdot10^{-6}$	0.266							$1.99\cdot10^{3}$	$9.30\cdot10^{-7}$	$3.32\cdot10^{-12}$
	I'	$8.61\cdot10^{3}$	$6.44\cdot10^{-6}$	$1.23\cdot10^{-12}$	$1.71\cdot10^{3}$	$5.80\cdot10^{-7}$	$5.14\cdot10^{-12}$	$3.44\cdot10^{-1}$	$1.42\cdot10^{-7}$	$1.65\cdot10^{-11}$	$8.79\cdot10^{3}$	$1.37\cdot10^{-6}$	$2.29\cdot10^{-11}$
Industrial region	$i=1$	$9.93\cdot10^{4}$	$6.51\cdot10^{-7}$	0.245							$9.93\cdot10^{4}$	$9.99\cdot10^{-7}$	$4.81\cdot10^{-13}$
	$i=2$	$1.11\cdot10^{3}$	$7.14\cdot10^{-7}$	0.666							$1.00\cdot10^{3}$	$7.84\cdot10^{-7}$	$6.43\cdot10^{-11}$
	$i=3$	$3.64\cdot10^{4}$	$2.48\cdot10^{-6}$	0.337							$3.64\cdot10^{4}$	$9.38\cdot10^{-6}$	$3.49\cdot10^{-11}$
	I'	$1.35\cdot10^{5}$	$6.72\cdot10^{-6}$	$1.12\cdot10^{-11}$	$1.41\cdot10^{3}$	$4.20\cdot10^{-6}$	$3.00\cdot10^{-11}$	$7.61\cdot10^{-1}$	$3.53\cdot10^{-7}$	$5.81\cdot10^{-11}$	$1.37\cdot10^{5}$	$1.12\cdot10^{-5}$	$9.87\cdot10^{-11}$
Stratospheric (20 km)	$i=1$				$4.49\cdot10^{0}$	$2.17\cdot10^{-5}$	0.248				$4.49\cdot10^{0}$	$5.10\cdot10^{-8}$	$8.34\cdot10^{-13}$
	$i=2$												
	$i=3$												
	I'	$4.07\cdot10^{-1}$	$3.36\cdot10^{-10}$	$9.54\cdot10^{-16}$	$4.10\cdot10^{0}$	$4.76\cdot10^{-8}$	$6.97\cdot10^{-13}$	$1.78\cdot10^{-2}$	$3.32\cdot10^{-9}$	$1.44\cdot10^{-13}$	$4.49\cdot10^{0}$	$5.10\cdot10^{-8}$	$8.34\cdot10^{-13}$

Note. n_i (i = 1, 2, 3) is the number concentration (in cm^{-3}) for the logarithmic-normal distribution of particles in different size ranges. The primed quantities indicate the additive contribution of various modes to the number (N', cm^{-3}), surface (S', cm^{-1}), and volume (V') particle concentrations in each size range indicated.

surface area, and volume. We shall therefore distinguish this type of distribution from the distributions of other parameters which will be discussed below.

The first continuous distribution of the number concentration with respect to size was proposed by Junge[9] in 1952 as a power function. This function was updated[10] in the following form:

$$dN(r)/d\lg r = n^*(r_0)(r/r_0)^{-\nu^*},$$

where $dN(r)/d\lg r$ is the density of the distribution of the number concentration, $N(r)$ the number concentration of particles with a radius greater than r, r the particle radius, r_0 an arbitrarily selected radius, $n^*(r_0)$ the density of the distribution for $r = r_0$, and ν^* the power exponent.

This formulation of the equation has the advantage that the distribution density has the dimensions of concentration despite the fact that it is the concentration density. The form of the distribution of particles with sizes in the range 0.1–10 μm is represented, according to this equation, by a straight line in terms of double logarithmic coordinates.

The advantage of this well known Junge distribution is its simplicity—only three parameters are used: the minimum radius r_0 of the fiducial recovery of the function, the coefficient $n^*(r_0)$ of the expression, and the power exponent $-\nu^*$. This distribution describes satisfactorily certain optical characteristics of the atmosphere.[11] Nevertheless, it does not describe the behaviour of the particles outside the range of their sizes indicated.

Studies carried out during the last two decades have yielded much new information about the distribution of the atmospheric aerosol with respect to size and this required a refinement of the formula describing the distribution.

At the beginning of the 1970's,[12] attempts were made to introduce for the description of the distribution with respect to size the Gaussian probability function related to the aerosol formation and transformation processes. As a result of this approach, certain particle size ranges were differentiated as "modes": nuclear, accumulation, and coarsely disperse.

Although the legitimacy of this approach is still questionable, the use of logarithmic-normal functions and their superposition leads to the following form of the equation for the distribution function:

$$\frac{dN}{d\lg r} = \sum_{i=1}^{3} n_i \frac{1}{\lg \sigma_i \sqrt{2\pi}} \exp\left\{-\frac{[\lg (r/R_i)]^2}{2(\lg \sigma_i)^2}\right\},$$

where $\lg \sigma_i$ is the degree of polydispersity of each logarithmic-normal distribution, R_i the average radius for each mode, and n_i the weight multiplier for the ith distribution.

In this equation, there are nine parameters but it can cover the entire range of sizes of the atmospheric aerosol—from 0.001 μm to several hundreds of microns.

The number distribution can be converted into a distribution with respect to the surface or volume (mass) of the particles, bearing in mind that

$$S = 4\pi r^2 \text{ and } V = {}^4/_3\pi r^3,$$

where S is the surface area of the sphere and V its volume.

Table 1 presents the parameters for all types of aerosol which are nowadays believed to be present in the atmosphere. The data quoted refer to the average relative humidity and a wind strength equal to 4 points on the Beaufort scale. Fig. 2 presents the corresponding types of distributions. The "polar" aerosol denotes particles of the layer near the Earth's surface in the Arctic and Antarctic regions.[13–15] The term "background tropospheric" aerosol is understood as the aerosol at heights above 5 km over dry land and above 3 km over the surface of oceans. This aerosol is fairly homogenous and occupies ~70% of the volume of the troposphere. The "background tropospheric" aerosol has been studied in mountain [observation] stations in air masses which move from above downwards and over the surface of oceans in order to exclude sea salt aerosol.[16–22] Together with sea salt aerosol, the background aerosol constitutes the "marine" aerosol. However, owing to the approximate nature of the averaging procedure, a claim of the type "marine aerosol – background aerosol = salt aerosol" is incorrect.[16,23,24] The term "background continental" aerosol refers to the aerosol in regions not subject to anthropogenic influences.[10,22,25] However, there is a minimal amount of information about this aerosol. The "dust sandstorm" aerosol was differentiated as a special type of natural aerosol in view of the enormous power of the source of these particles, their ability to travel over long distances, and their possible influence on the climate.[24,26,27] The "aerosol in agricultural regions"[10,28–30] near populated agricultural areas as well as the "aerosol in industrial regions",[10,29] formed as a result of anthropogenic influences, have been differentiated as separate types. The "stratospheric aerosol" differs from all the types indicated above by the fact that it is described by a unimodal logarithmic-normal distribution and is fairly monodisperse.[31] It is noteworthy that, after volcanic eruptions, the concentration of particles in the layer of stratospheric aerosol is a maximum but then rapidly diminishes.[32] The data presented on the stratospheric aerosol refer to a height of 7 km above the tropopause and the samples were taken one year after volcanic eruptions during the period between 1970 and 1981. This type of distribution is in fact to be expected bearing in mind the ageing effect and the long residence time of the particles in the stratosphere.

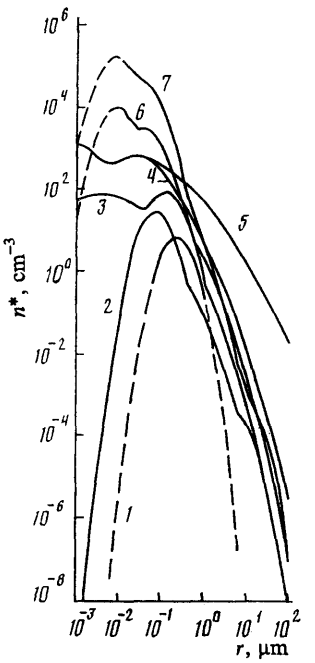


Figure 2. Distribution of the number concentrations of different types of aerosol in the form of the dependence of $dN/d\lg r$ on the particle radius. Type of aerosol: (*1*) stratospheric; (*2*) polar; (*3*) background tropospheric; (*4*) background continental; (*5*) desert sandstorm aerosol; (*6*) aerosol from agricultural regions; (*7*) aerosols from industrial regions.

Fig. 2 illustrates interesting features in the size distribution of the particles of different aerosols. The polar and stratospheric aerosols have fairly narrow, monodisperse distributions typical for "aged" aerosols. Therefore, in this case, on passing from the number distribution to the surface or volume distribution, the form of the distribution does not change while the average radius undergoes a slight alteration. The dust storm aerosol differs from the background continental aerosol only by the higher concentration of particles whose size exceeds 0.1 μm and such particles constitute the main bulk of the aerosol. Although in dust storms the number concentration of the Aitken particles exceeds very slightly that for the particles of the background continental aerosol,[24] their mass concentration is much higher.

The background tropospheric aerosol is of great interest. It has been suggested[33] that this aerosol represents the aged continental background aerosol with a number concentration of ~300 particles cm^{-3}. Indeed, the number concentration is of this order of magnitude but the form of the distribution of the background tropospheric aerosol shows that in this case a continuous gas–particle transformation process takes place, since the fraction of fine particles is high. It is unlikely that such an aerosol is "aged". Similar gas–particle transformation processes have been observed for the background continental aerosol and also for aerosols from agricultural areas and industrial regions. This was in fact to be expected. However, it is essential to note that the distribution of these submicron particles with respect to size has been inadequately studied and further investigations are needed. The concentration of the aerosol with particles larger than 0.1 μm diminishes with increase in the particle radius, as predicted by the Junge distribution. On passing to the distribution of the particles with respect to volume, the distribution function assumes the form of a fairly even plateau and in the determination of the mass of the aerosol this range of sizes is therefore most important, while the Aitken particles make an insignificant contribution.

In conclusion yet another important remark has to be made. For all types of aerosols, the most significant differences in the form of the distribution are observed in the case of the finest and largest particles. For particles of intermediate size, such differences are insignificant. It seems that this finding confirms the earlier hypothesis of a relationship between the lifetime of the aerosol and the fluctuations in its parameters: the maximum variations occur for particles with a minimal lifetime in the atmosphere.

Fig. 2 does not present the confidence intervals for individual distributions. The latter are therefore in no way a result of a large number of averaging steps but are rather a result of certain hypotheses and approximations based on the few published data. The main reason for the deficiency of information is the enormous experimental difficulty of measuring the distribution of particles over the entire range of sizes. Much still remains to be done in this field in the future.

IV. Dependence of the properties of the aerosol on the particle size

In this section we shall not discuss the properties of the aerosol which can be readily calculated from the particle distribution function with respect to size, such as the rate of deposition, mobility, and others, but shall concentrate attention on the measurable properties of the aerosol. The parameters describing the distribution of these properties are important for all types of aerosols and not only for the atmospheric aerosols. The majority of these parameters are calculated on the assumption that the aerosol particles are spherical.

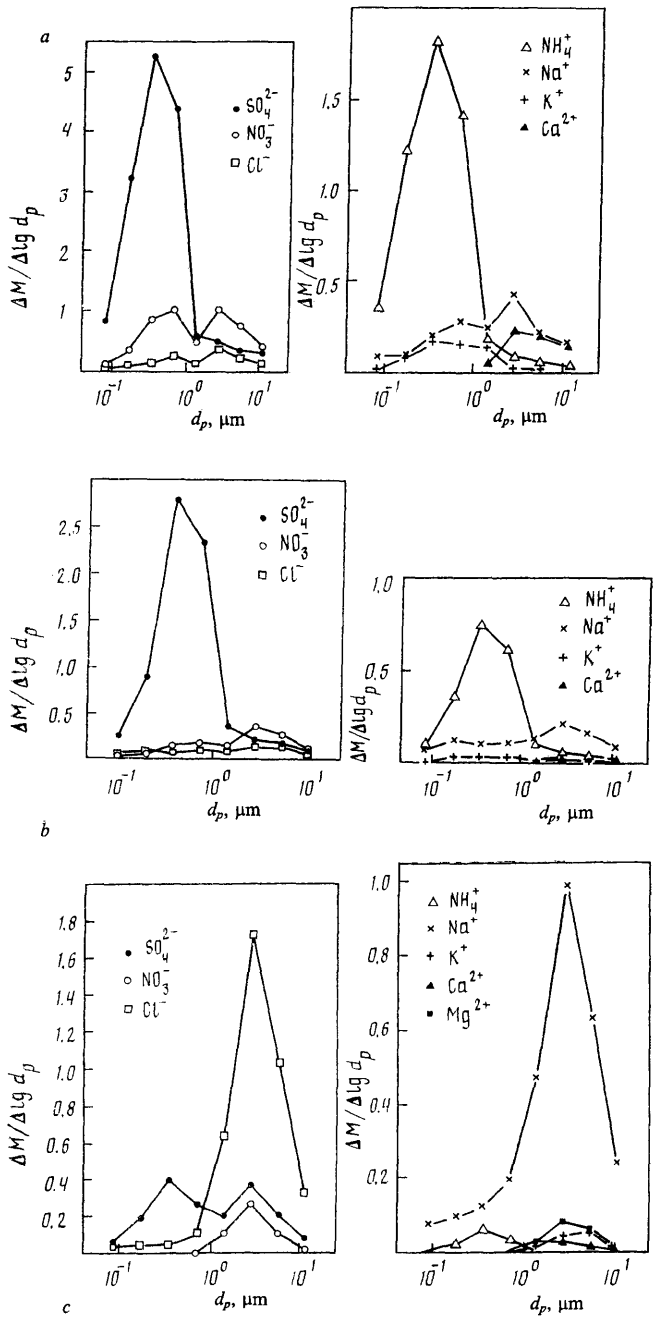


Figure 3. Differential mass distribution of the aerosol $\Delta M/\Delta \lg d_p$ (μg m^{-3}) with respect to size (diameter d_p, μm) of the most widely distributed ions for industrial (*a*), marine (*b*), and background continental (*c*) types of aerosol.[37] Data obtained using impactors.

In order to investigate the distribution of any kind of properties of the aerosol, it is essential to know the size distribution of the particles. In most cases, in order to be able to investigate properties of the aerosol such as the elemental or ionic composition, it is necessary to accumulate a sufficient mass of the substance. Such accumulation usually requires a long time (several days or even weeks). During this period, the aerosol can change or can be contaminated by impurities from local random sources. In order to avoid this and to obtain reliable results, it is necessary to exercise much caution. One of the ways of avoiding such faults, involves a decrease in the sampling time although it is then sometimes necessary to sacrifice information about the size distribution of particles. The distribution function is very frequently not measured and only the overall mass concentration of the aerosol, its overall chemical composition, or the content of only one chemical compound are investigated. Investigators sometimes restrict their study to only specific particles, for example, giant aerosol particles. The main bulk of the substance of the aerosol is very frequently concentrated in such particles.

One should always remember, particularly in the study of the dependence of the elemental or chemical composition of the aerosol on the particle size, that the aerosol has a mixed composition.[34] It is necessary to distinguish external and internal mixing of the chemical composition. By external mixing, one understands the presence of a multiplicity of particles having different chemical compositions, each particle consisting of one pure substance or specific set of compounds, determined by the source of the aerosol, for example, ammonium sulphate of sea salt. Internal mixing describes various stages of the disappearance of this "purity", which leads ultimately to the formation of a mixture of substances in each particle. Evidently particles of the first type are encountered only in the vicinity of specific sources of the aerosol, while those of the second type are a result of a secondary transformation of the aerosol (ageing). In describing the chemical composition of a mixed aerosol, the authors frequently do not indicate how the reported results have been treated. Evidently the content of any substance in the aerosol can be represented by the dependence on the effective size of a particle seemingly consisting of only the given pure substance or by the dependence on the true size of the particle (containing also other substances) whose composition includes the given compound.[35] The concentration of ions and not chemical compounds is more frequently quoted.

The first studies of the dependence of the ionic composition of large and giant aerosol particles on their size were carried out in 1953.[36] Fig. 3 illustrates the dependence of the concentration of sulphate ions on the size of aerosol particles. The data were obtained at a [research] station in an agricultural locality in the Federal Republic of Germany. This dependence has several maxima in the range of sizes 0.1 – 10 μm. Their positions coincide with the positions of the maxima in the distribution of the mass concentration of the NH_4^+ ions, which confirms the claim that the most widely distributed water-soluble compound in aerosols is ammonium sulphate. The maxima in the distribution of the concentrations of other ions investigated (K^+, Na^+, Ca^{2+}, NO_3^-, and Cl^-) are in the range of sizes 1 – 10 μm.

Similar measurements have been carried out in England for the marine aerosol and the aerosol from industrial regions.[38] If the contents of cations and anion are compared with aerosol particles whose sizes are in the range 0.1 – 1 μm, a deficiency of cations is observed. It seems to the author that the main cation which was not taken into account in these investigations was H^+. The above hypothesis has also been confirmed by studies of other investigators.[39] Hence one may conclude that the atmospheric aerosol should possess acid properties.

The most widely distributed ions over the surface of oceans are sodium and chloride ions. The maximum in their mass distribution lies in the range of aerosol sizes 1 – 10 μm. It is most likely that these are water droplets containing sea salt. It would appear that exactly the same distribution should have been observed also for the NH_4^+ and SO_4^{2-} ions if the origin of ammonium sulphate had been similar. However, sulphate ions are mainly supplied by aerosol particles with sizes in the range 0.1 – 1 μm brought from the continents (the so called "excess" sulphates[40]). Only one communication[16] reports the distribution of ammonium sulphate over the entire range of sizes of aerosol particles. The number distribution of the $(NH_4)_2SO_4$ concentration has a distinct maximum in the range of sizes 0.01 – 0.1 μm, after which the concentration of the sulphate diminishes with increase in particle size. If one goes over to the differential mass distribution, then a second maximum appears in the range 0.1 – 1 μm (the results were obtained from an electron microscope analysis of the morphology of the particles). These data are open to some doubt because the ammonium sulphate particles can vaporise *in vacuo* during preparatory operations.

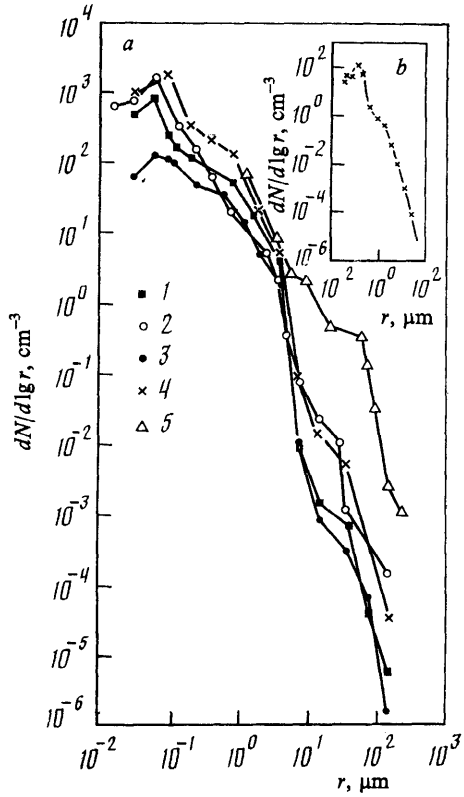


Figure 4. Differential distribution function of the number concentration of the mineral aerosol from the Sahara desert with respect to size (*a*). Data obtained by taking samples on filters in Mali (*1* and *2*), Senegal (*3* and *4*), and Libya (*5*). The inset (*b*) shows the distribution for the aerosol over the Atlantic ocean:[16] (*1*) and (*3*) pure air; (*2*) and (*4*) dust containing air; (*5*) dust storm.

Table 2. Mass concentrations of substances in the aerosol according to X-ray diffraction data.

Step (D_{50}, μm)	QU	CA	DOL	GYP	FELD	NaCl	AmCl	AmS	AmS2N	AmS3N	CaAmS	PbAmS	LET	TSP	%XTAL
A (2)	0.87± 0.53 (6)	1.47± 0.89 (6)	0.98± 0.71 (6)	0.03± 0.07 (1)	0.86± 0.50 (6)	0	0	0	0	0	0	0	0	10.2± 5.8 (6)	43±8 (6)
B (0.65)	0.30± 0.18 (6)	0.48± 0.28 (6)	0.29± 0.16 (6)	0.09± 0.18 (2)	0.21± 0.23 (4)	0	0.01± 0.02 (1)	0.16± 0.25 (2)	0	0	0.18± 0.27 (3)	0	0.03± 0.07 (1)	3.9± 1.8 (6)	44±8 (6)
C (0.37)	0.04± 0.04 (4)	0.12± 0.18 (2)	0.03± 0.04 (2)	0.02± 0.04 (1)	0	0	0	0.96± 1.2 (6)	0.25± 0.22 (4)	0	0.08± 0.10 (3)	0.008± 0.20 (1)	0.14± 0.22 (2)	3.2± 2.3 (6)	57±14 (6)
F (<0.37)	0.17± 0.11 (5)	0.36± 0.24 (5)	0.11± 0.12 (5)	0	0	0	0	2.22± 1.52 (6)	0	0	0.32± 0.49 (2)	0.14± 0.13 (4)	0.20± 0.33 (2)	8.8± 4.4 (6)	47±19 (6)
Sum of specimens	1.37± 0.67 (6)	2.43± 1.42 (6)	1.41± 0.89 (6)	0.13± 0.21 (2)	1.07± 0.71 (6)	0	0.01± 0.02 (1)	3.36± 2.9 (6)	0.25± 0.22 (4)	0	0.58± 0.51 (5)	0.14± 0.13 (4)	0.38± 0.60 (2)	26.2± 14 (6)	46±10 (6)

Overall content of ions

SO_4^{2-}: 3.3±1.9 (1.6–7.0) n=6 (34 nequiv. m^{-3})
NO_3^-: 0.21±0.29 (0–0.8) n=4 (3 nequiv. m^{-3})
NH_4^+: 1.1±0.70 (0.5–2.5) n=6 (61 nequiv. m^{-3})
Cl^-: 0.004±0.01 (0–25) n=1 (0.1 nequiv. m^{-3})
CO_3^{2-}: 1.7±1.1 (0.7–4.2) n=6 (28 nequiv. m^{-3})

Note. The aerosol was collected in April–June 1986 on the outskirts of Toronto (Canada). The arithmetical-mean mass concentrations and standard deviations (in μg m^{-3}) are presented. The number of measurements on which the averaging is based is indicated in brackets. The steps of the impactor are designated by the letters *A*, *B*, and *C* (*F* is the output filter). Abbreviations: QU = quartz, CA = calcite, DOL = dolomite, GYP = gypsum, FELD = feldspar, NaCl = halite, AmCl = NH_4Cl, AmS = $(NH_4)_2SO_4$, AmS2N = $(NH_4)_2SO_4.2NH_4NO_3$, AmS3N = $(NH_4)_2SO_4.3NH_4NO_3$, CaAmS = koktaite, PbAmS = $PbSO_4.(NH_4)_2SO_4$, LET = letovicite, TSP = total suspended particles, and %XTAL = percentage fraction of substances analysed by X-ray diffraction.

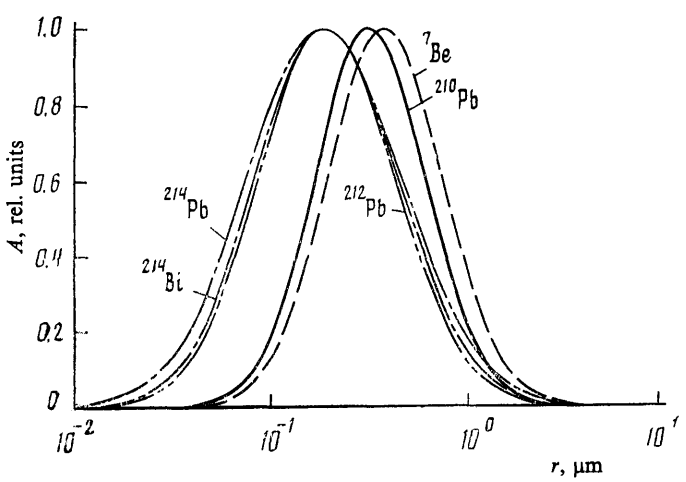


Figure 5. Dependence of the radioactivity *A* (in arbitrary units) on the radius of aerosol particles (for natural radionuclides).

The dependence of the concentrations of ions such as Br^-, Mg^{2+} [39] as well as substances of mineral origin (Al_2O_3, SiO_2, Fe_2O_3, CaO) on the particle size is not described in the literature. The dependence of the composition on particle size is also not available for the organic aerosol.

The distribution of water-insoluble minerals with respect to particle size has been reported.[27] Fig. 4 illustrates the number distribution of the continental aerosol compared with the marine aerosol. In all cases the maximum in the distribution is observed for particles with a radius less than 0.1 μm. The decrease in concentration with increase in particle radius is non-monotonic. On passing to the mass distribution, maxima arise in the range of sizes 1–10 μm, 10–100 μm, and higher.

The first studies on the distribution of minerals with respect to particle size in the continental aerosol have been reported.† Table 2 presents the results of the analysis of specimens selected in the Spring and in the Summer. It was established that minerals constitute ~50% of the mass of the aerosol. These compounds are present over the entire range of particle sizes.

The natural radionuclides entering the atmosphere are rapidly adsorbed on aerosol particles and, since such adsorption is due to diffusion, the distribution of the radioactivity of the aerosol depends on its distribution with respect to the size and surface area of the particles. Although theoretical calculations predict that the maximum radioactivity should be observed for particles whose size is about 0.1 μm, the latest results of the study of the distribution of the

†W T Sturgess, R M Harrison *Atmos. Environ.* 1989, **23**, 1083–1098.

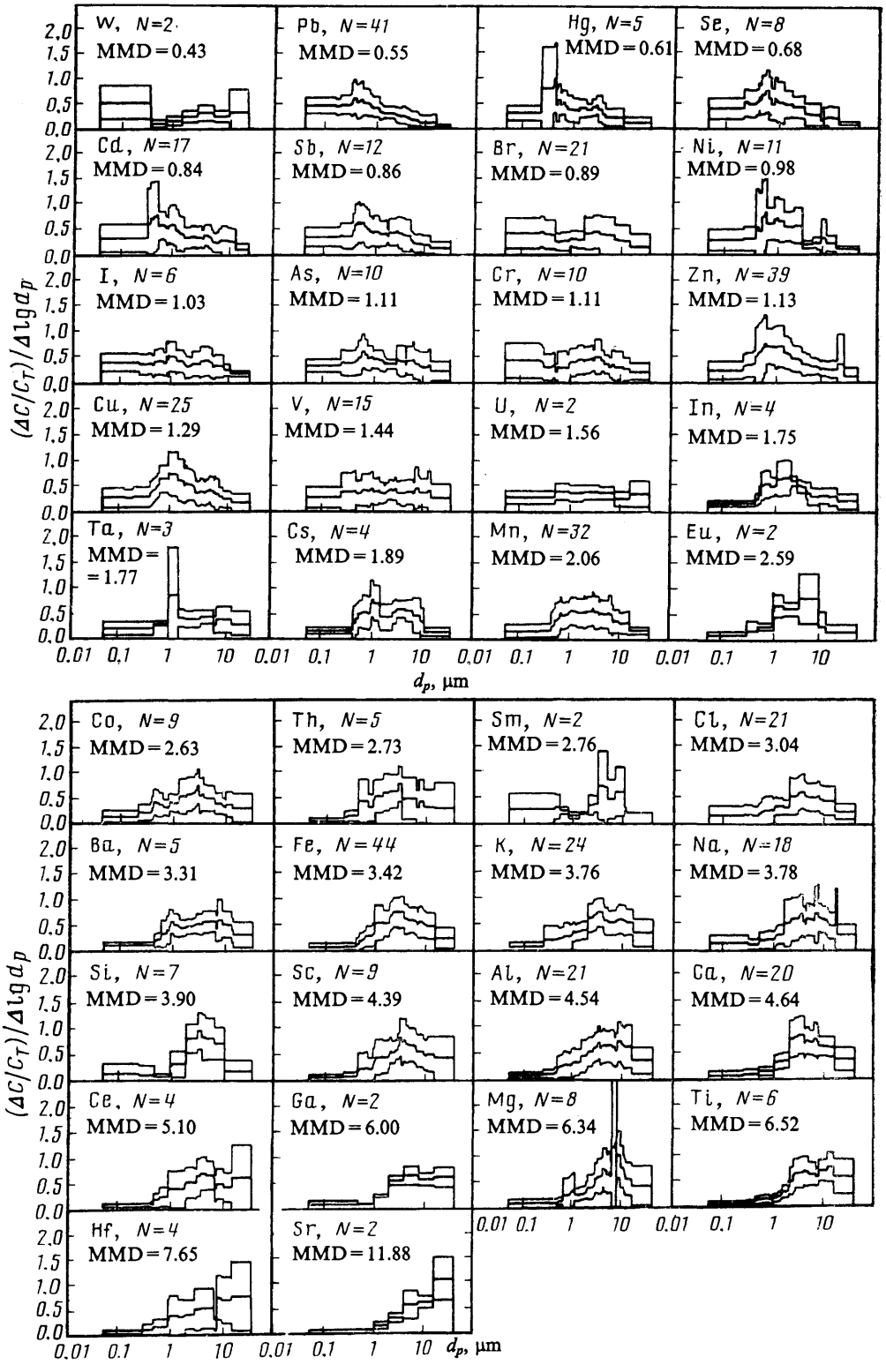


Figure 6. Normalised differential mass distributions for 38 microelements. The data (central line) are presented together with standard deviations (upper and lower lines). *N*—number of averaged distributions; MMD—median mass diameter d_p.[43] The distributions are arranged in order of increasing MMD.

radioactivity of ^{214}Pb and ^{212}Pb in the aerosol from agricultural and industrial regions show[41] that the maximum radioactivity is observed for particles whose radius is about 0.2 μm and in the case of the radioactivity of ^{7}Be and ^{210}Po for particles with a radius of 0.4 μm (Fig. 5). The size distribution for the isotopes formed during tests of nuclear weapons has not been analysed.

Biological aerosols have so far been rarely differentiated as a separate type. Such aerosols contain not only pollen, spores, and bacteria (living organisms) but also ground up pieces of plants and insects and in general decomposing organic material. Pollen, spores, and bacteria are very often considered separately from other types of aerosol. These particles are fairly monodisperse. The distribution of the biological aerosols with respect to the sizes of particles having a radius greater than 2 μm has been investigated.[42] It was found that during Summertime the number concentration of the biogenic aerosol in agricultural localities within the Federal Republic of Germany is between 20 and 40% of the total number concentration of the aerosol.

The aerosol particles can carry an electrical charge, forming the so-called large ions. Ideas concerning the electrical properties and the distribution of large ions have not changed significantly compared with the 1930's. However, the study of these "ionic" spectra has in fact led ultimately to the concept of a continuous distribution of particles with respect to size.[9]

Investigators have devoted much attention to the microelemental composition of the atmospheric aerosol. There are numerous data on this question. A fairly detailed review[43] quotes 38 elements as present in their aerosol particles with diameters ranging from 0.05 to 40 μm (Fig. 6). The curves for the distribution of the elements with respect to particle size for aerosols collected at different times (over a period greater than 20 years) and by different methods (each of which has its limitations) agreed fairly well as regards their shape. A small number of distributions have a fairly monodisperse character (for example, for Mg and Ta). (Naturally, only in the case of distributions of this kind does a parameter such as the median mass diameter have a physical significance.) On the other hand, the majority of distributions are polydisperse without a distinct average radius. A typical example here is provided by vanadium. Elements for which less than two distributions are known from the literature are not considered in this list. Microelements such as sulphur are also not included, since they could not be determined by the methods employed (neutron activation analysis, X-ray fluorescence, and proton-induced X-ray emission).

V. Horizontal or geographical distribution of the aerosol

The distribution of the global atmospheric aerosol is subject to appreciable fluctuations in view of its short lifetime. This is particularly notable if one considers the two hemispheres. Thus the time required for the exchange of the atmospheric aerosol between the Southern and Northern Hemispheres is of the order of two years. This exchange time is significantly greater than the lifetime of the aerosol and it is therefore unlikely that any aerosol particles from the Northern Hemisphere could enter the Southern Hemisphere. In order to achieve a reliable statistical study of the expected fluctuations in the aerosol characteristics, an enormous number of measurements are necessary. Clearly, such a large volume of information can be obtained only for certain parameters of the aerosol and for the majority of the parameters data concerning the distribution of the particles with respect to size are lacking.

An approximate idea about the distribution of the aerosol in space can be obtained by considering the data in Tables 1 and 2 where the characteristics of the polar and background continental aerosols, the dust sandstorm aerosol, as well as the aerosols from agricultural and industrial regions are presented. Fig. 7 illustrates the overall number, surface, and volume concentrations of particles in order of increasing number concentrations. In most cases, these quantities are correlated. The dust sandstorm aerosol is an exception. Whereas the surface area and volume of this aerosol are much higher, the number concentration remains comparable to the number concentration of the particles of the background continental aerosol. The total areas and volumes of the agricultural and background continental aerosols are comparable, but the number concentration of the particles in the agricultural aerosol is significantly higher, which indicates a greater strength of the gas–particle transformation.

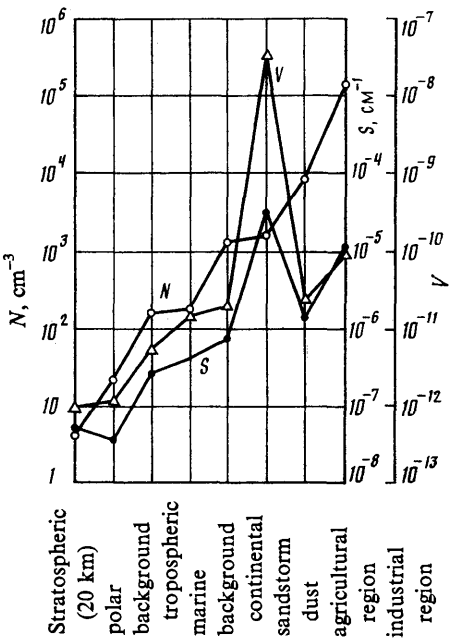


Figure 7. Total number (N), surface (S), and volume concentrations for the types of aerosol presented in Table 1 (in order of increasing number concentration of the particles).[3]

When the detailed distribution in space is described in the literature, the treatment is confined to homogeneous localities. Apparently the authors feel more confident when selecting data on the assumption that a fairly homogeneous source of the aerosol is present or a fairly homogeneous mechanism for the removal of the particles from the atmosphere operates.

Fig. 8 presents a map of the distribution of the number concentration of the condensation nuclei (Aitken particles) over the ocean. Evidently, in the central regions of the oceans the

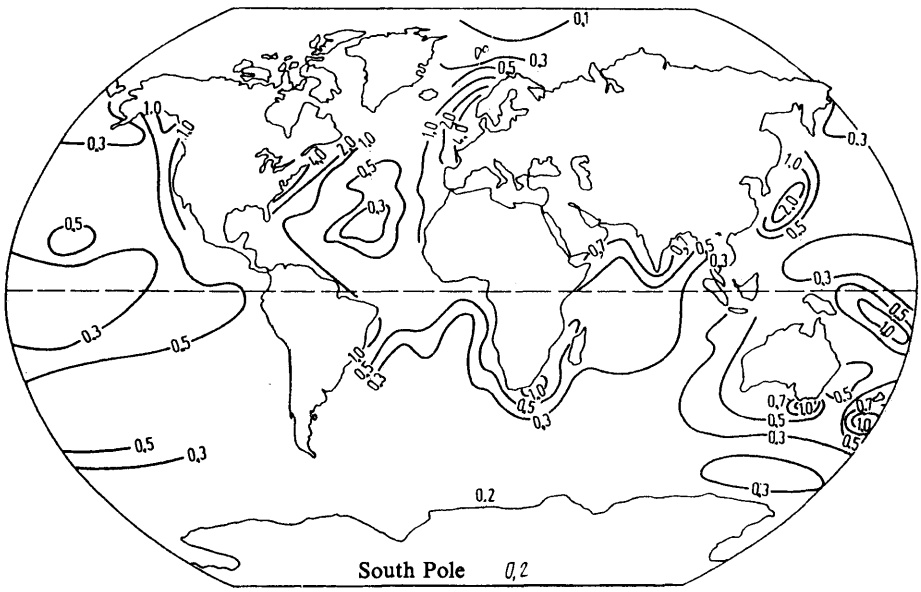


Figure 8. Map of the distribution of the average concentration of Aitken nuclei (10^3 cm^{-3}) over the surface of the oceans. Data taken from Jaenicke[3] and Podzimek.[44]

concentration of Aitken particles diminishes. This does not conflict with the seasonal maps published in 1966 for particles of sea salt greater than 0.7 μm.[45] The data were calculated on the basis of a climatic atlas of the world[46] using the relation between the mass concentration of these particles, transported by air, and the percentage frequency of the repetition of winds with a specified force. One may conclude that the map reflects the storm activity of the oceans. It can be refined by using new data for the relation between the mass concentration of sea salt particles and the wind strength.[3] A similar map can be plotted by using the published[3] relations between the mass concentration of the mineral dust and the wind velocity in the desert. We may note that the mass concentration of this dust is approximately 10 times greater than the mass concentration of the oceanic aerosol.

A minimum concentration of the aerosol (Fig. 8) is observed in polar regions. This was in fact to be expected, since the principal aerosol sources are absent here. The concentration of the particles increases when approaching the continents, which are active sources of aerosol. A more detailed map has been published for the Arctic part of Europe,[13] showing that the average concentration of the aerosol is below 300 particles cm^{-3}. Near populated areas and territories, subject to anthropogenic activity, the concentration of aerosol is higher.

In many industrial countries, the parameters of atmospheric pollution, including certain characteristics of the atmospheric aerosol, are measured at meteorological stations. This is done mainly in order to avoid the formation of smog, acid rain, and the destruction of forests. Thus, using a network of meteorological stations, the extinction coefficients have been calculated for the surface air in the eastern part of the USA.‡ As early as 1948, an increase in the number of sites where the surface air has high extinction coefficients was observed. During the period 1970–1974, a high value of this coefficient was noted for regions along the Great Lakes and the urban conurbation on the Atlantic littoral. As one moves West, the extinction coefficient falls.

‡R B Husar, D E Patterson, J M Holloway 4th Symposium on Atmospheric Turbulence, Diffusion and Air Pollution. Reno, NV, USA, 1979.

Table 3. Concentrations (μg m^{-3}) of organic substances of different classes in certain types of aerosol at the standard pressure and temperature.[3]

Substance	Marine aerosol		Background continental aerosol	Aerosol from agricultural regions	Aerosol from industrial regions
	Northern Hemisphere	Southern Hemisphere			
Total organic carbon	0.60	0.36	1.1	2.5	
Aliphatic neutral substances	0.29		0.26	0.53	6.8
Aromatic neutral substances	0.25	0.25	0.12	0.26	3.1
Polar neutral compounds	0.16		0.20	0.35	4.9
Acids	0.29	0.18	0.20	0.70	10
Bases	0.08	0.09	0.03	0.20	2.0
Total hydrocarbons ($>C_{15}$)	0.014		0.14		0.27
Normal aliphatic acids and ketones	0.09		0.27		0.27
Normal aliphatic alcohols			0.83		1.64
Formaldehyde	0.0054			0.041	

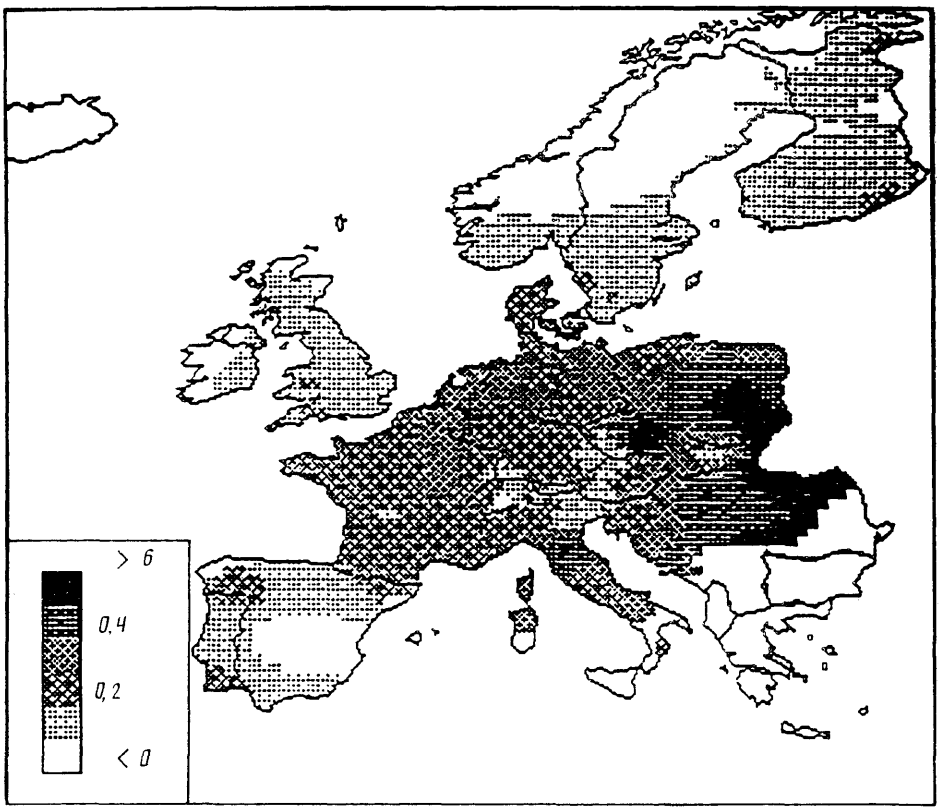


Figure 9. Map of the distribution of SO_4^{2-} in aerosols (in μg S m^{-3}) based on measurements within the framework of the combined program on the monitoring and evaluation of the large scale transport of pollutants in the atmosphere (EMEP).[47]

A map of the distribution of sulphates as aerosol over certain regions of Europe was published recently.[47] Fig. 9 shows that the concentration of sulphate is low over the sea littoral of northern Europe and the Mediterranean and is high in the eastern part of the continent.

The study of organic compounds in the aerosol is extremely difficult because of the great variety of these substances and their low concentration. Concentration data are available for only 95 compounds out of more than 1000 present in the marine and background continental aerosols.[3] Table 3 presents the concentrations of organic compounds of different classes in the marine aerosol of the Southern and Northern Hemispheres, the background continental aerosols and in the aerosols of the agricultural and industrial regions. The contents of organic substances in the marine aerosol and the aerosol from industrial regions differ by ~2 orders of magnitude.

VI. Vertical distribution of the aerosol

The types of distributions presented above show approximately, in relation to the background tropospheric and stratospheric aerosols, how the distribution of the particles with respect to size can vary with height.

As regards the distribution of the aerosol with respect to size as a function of the height over sea level, such studies have only just begun. Measurements performed over the Pacific Ocean in the course of the GAMETAG experiment[48] are most probably subject to instrumental errors. In the continental part of the USA, impactors for the study of the size distribution of the aerosol (in the range of particle sizes 0.2–3 μm) were inserted into the troposphere at heights up to 9 km. Fig. 10 presents data for the size distribution of the particles. At low altitudes, the concentration of the aerosol diminishes with increase in the particle radius. In the free troposphere, this decrease in concentration is modulated. This fact indicates a change in the form of the size distribution of the aerosol from that typical for the background continental aerosol to one characteristic of the background tropospheric aerosol.

The vertical distribution of the sea salt aerosol has been studied up to the height of the cloud cover (~1000 m).[50] The mass concentration of the salt diminishes from 2 mg m^{-3} in the layer where large spray particles are present (at a height of 0.1 m) to 1 μg m^{-3} at an altitude of 2000 m. A similar inversion of the salt layer under the cloud layer is a fairly common phenomenon. Above the cloud layer, the concentration of sea salt is so low that it is not susceptible to measurement.

A cross-section of the spatial distribution of the mass concentration at an altitude of 5.5 km from the South Pole to the North Pole was constructed for the tropospheric background aerosol.[3] At this altitude, the average concentration of the aerosol in the Southern Hemisphere is less than 0.3 μg m^{-3}. The maximum in the mass concentration is observed between 40 °S and 50 °S and amounts to 2.2 μg m^{-3}. In Arctic regions, the concentration of the aerosol is 1 μg m^{-3}.

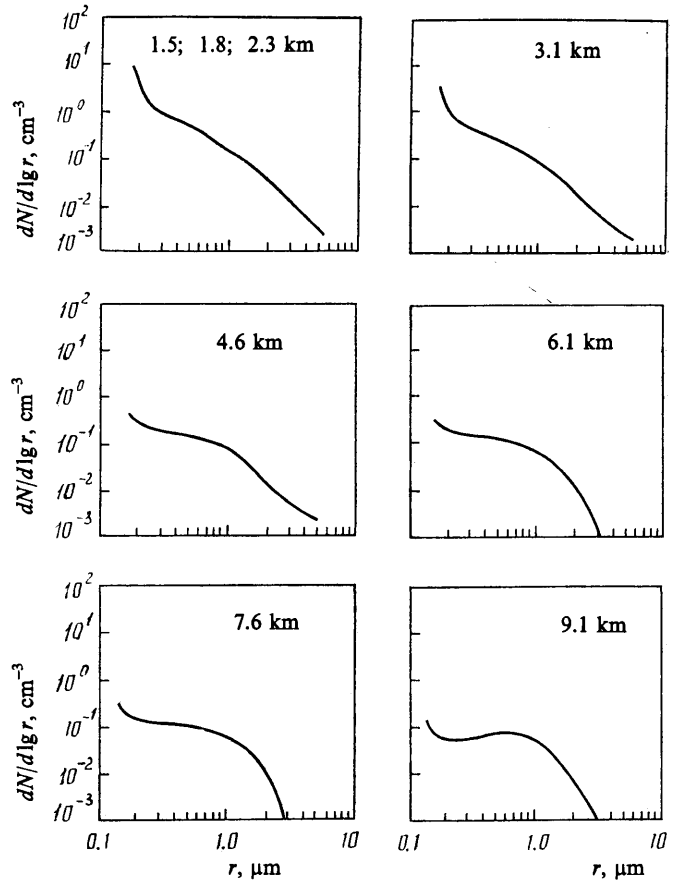


Figure 10. Average distribution functions for the number concentration of the aerosol at different heights in the continental part of the USA.[49]

A vertical section through the distribution of the number concentration of the aerosol was constructed in 1972–1973[51] and is shown in Fig. 11. One can easily note the decrease in the concentration of particles on moving from the surface of the Earth to the tropopause. In the stratosphere there is a layer with the distinctly enhanced concentration of particles. This so called "Junge layer" or the "sulphate layer" is located approximately 7 km over the tropopause. The concentration of the aerosol in this layer is a maximum over the equator. During periods of high volcanic activity, particles enter the Junge layer directly from the volcanic eruptions and this layer then undergoes marked changes. These changes were manifested particularly strikingly in a lidar study of the vertical distribution of the background scattering coefficient before and after the eruption of the El Chichon volcano (Mexico) in 1982[52] (Fig. 12).

The Junge layer continues to exist also during the period of low volcanic activity. During this time, it consists mainly of sulphuric acid particles, formed mainly as a result of the gas–particle transformation from dimethyl sulphide, which is the gaseous tropospheric precursor of H_2SO_4.[53] This layer has been thoroughly investigated from satellites and by terrestrial lidars, because it influences the transparency of the atmosphere, which is an important factor for the Earth's climate. Polar stratospheric clouds are part of this layer, influencing the geochemical ozone cycle and determining the dynamics of the development of the Antarctic ozone hole.

The vertical distribution of the mass concentration of the aerosol over deserts is naturally different. As already reported, mineral particles are distributed uniformly up to a height of ~6 km and this is probably characteristic of all deserts.

The vertical distribution of the number concentration of Aitken particles differs significantly from that for the majority of other particles. In it, there is no distinct layer in the stratosphere. The concentration of these particles diminishes with increased altitude and assumes a value of 1–10 particles cm^{-3} in the middle stratosphere.[54] The number concentration of condensation nuclei

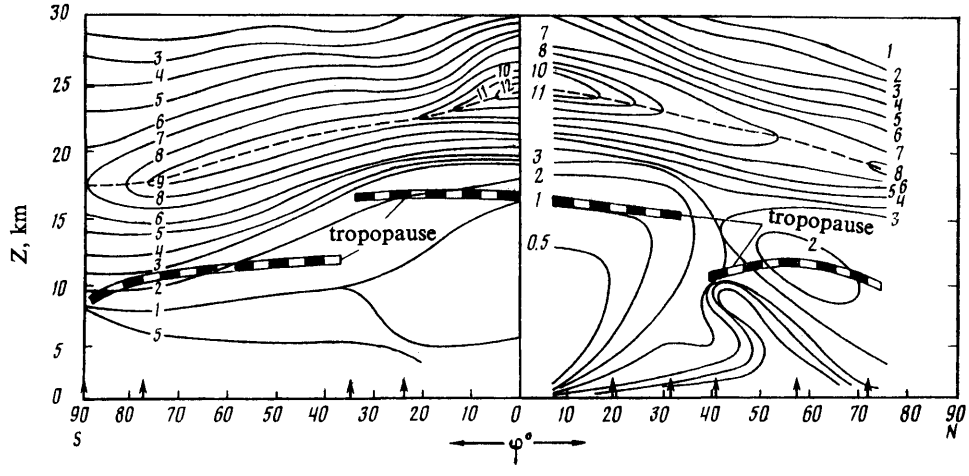


Figure 11. Number concentration contour lines for aerosol particles larger than 0.15 μm in radius as a function of the geographical latitude and height above sea level. The data refer to the period 1972–1973.[51]

increases only for a short time after volcanic eruptions.[55] Fig. 13 illustrates typical examples of the distribution of these particles.

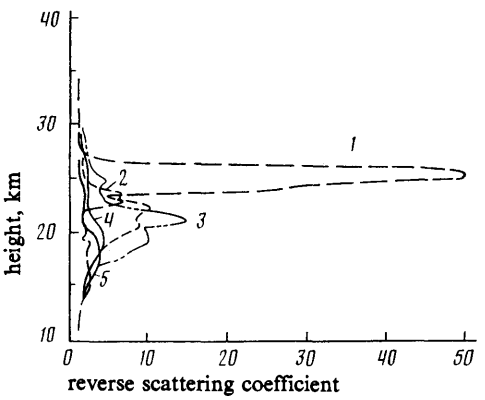
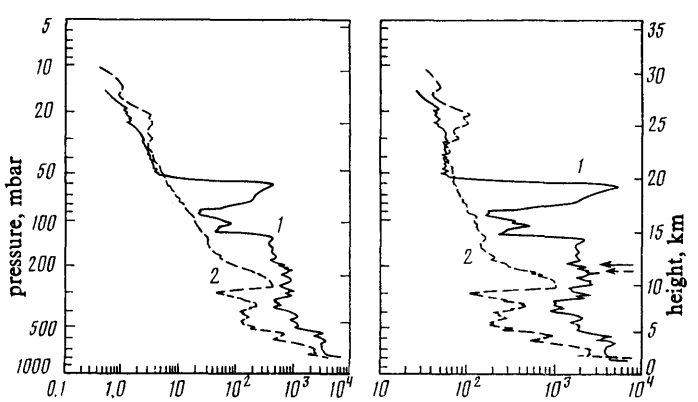


Figure 12. Vertical distribution of the coefficient of backward scattering obtained in terrestrial lidar studies in the region 37 °N, 76 °W. Probing laser wavelength—0.6943 μm:[52] (*1*) data for 1st July 1982; (*2*) data for 27th October 1982; (*3*) data for 3rd January 1983; (*4*) data for 30th June 1983; (*5*) data for 8th November 1983.



concentration of condensation nuclei, no. of particles in 1 mg of air

cm^{-3}

Figure 13. Vertical distribution of the concentration of condensation nuclei before and after the eruption of the volcano on the island of St. Helena.[55] The arrows indicate the position of the tropopause: (*1*) data for 20th June 1980; (*2*) data for 12th November 1979.

VII. Conclusion

In the last decade, our knowledge about the global distribution of the atmospheric aerosol increased immeasurably. Nevertheless, it is seen from the present review that we still know too little about it. A complete global map cannot be drawn for any one individual parameter of the aerosol and we are therefore forced to make do with incomplete information. This situation is unsatisfactory at a time when problems of vital importance for humanity, such as the changes in the climate and in the air require a detailed understanding of the state of the atmosphere, including the aerosol. The global computer meterological and climatic models suffer particularly from the deficiency of information about the distribution of the aerosol. Hitherto the question of the influence of the aerosol on the climate has given rise to controversy. Nevertheless, it may be that the facts presented in this review will inspire investigators to fill the existing gaps.

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Catalytic methods for lowering the amount of nitrogen oxides in exhaust gases on combustion of fuel

Z R Ismagilov, M A Kerzhentsev, T L Susharina

ABSTRACT. The catalytic methods for reducing the amount of nitrogen oxides in exhaust gases on combustion of different types of fuel are analysed: the catalytic combustion method and the method involving the selective catalytic reduction of nitrogen oxides by ammonia.

The bibliography includes 187 references.

Contents

I. Introduction 973
II. Sources of nitrogen oxides in fuel combustion processes 973
III. Selective catalytic reduction of nitrogen oxides by ammonia 974
IV. Catalytic combustion as a method of preventing the formation of nitrogen oxides 978

I. Introduction

Nitrogen oxides NO_x (NO and NO_2) are some of the most dangerous contaminants of air. Extremely low maximum permitted concentrations (MPC) have been established in all industrially developed countries for these compounds, which have a pronounced general toxic and irritant activity. Together with sulphur oxides, nitrogen oxides make a large contribution to the formation of acid rain, which leads to the destruction of forests, the poisoning of water reservoirs, and the formation of smog[1].

Considerable amounts of NO_x (up to 770 million tonnes annually) are formed as a result of natural processes—nitrification, forest fires, and storms. As a result of human activity, about 60 million tonnes of NO_x (calculated as NO_2) is produced annually[1,2], but anthropogenic waste is concentrated, in contrast to natural ones, in populated regions and lead to high local ground level NO_x concentrations. The principal sources of nitrogen oxides in industrially developed countries are power generation and transport, giving rise to approximately 95% of NO_x waste, the contribution of chemical industry being less than 5% [2]. Thus the principal amount of anthropogenic NO_x is produced as a result of the combustion of gas, petroleum fuel, coal, and other solid fuels. Further increase in the amount of NO_x waste can lead to irreversible ecological consequences on a global scale and therefore questions concerning the reduction of the amount of such waste are of extremely great current interest. A combined approach, including both the purification of smoke gases and the reduction or prevention of the formation of NO_x in combustion processes is required for the solution of this problem.

II. Sources of nitrogen oxides in fuel combustion processes

Nitrogen oxides can be formed on combustion of fuel both from atmospheric nitrogen ("thermal" and "fast" NO_x) and from bound nitrogen forming part of the composition of nitrogen-containing compounds ("fuel" NO_x).

1. Thermal nitrogen oxides

Thermal nitrogen oxides are formed as a result of the high-temperature oxidation of atmospheric nitrogen via Zel'dovich's radical chain mechanism[1,3]:

$$O_2 + M \overset{k_1}{\rightleftarrows} 2O + M, \quad (1)$$

$$N_2 + O \overset{k_2}{\rightleftarrows} NO + N, \quad (2)$$

$$O_2 + N \overset{k_3}{\rightleftarrows} NO + O, \quad (3)$$

where M is any species. Reaction (3) proceeds much faster than reaction (2) and the rate of formation of NO is therefore specified by the equation

$$\frac{d[NO]}{dt} = 2k_2[O][N_2] = k_{eff}K^{1/2}[O_2]^{1/2}[N_2],$$

where $k_{eff} = 2k_2$ is the effective rate constant and K is the equilibrium constant of reaction (1).

The temperature dependence of the yield of thermal NO_x is exponential. In the temperature range characteristic of the flame combustion of fuel in air (1800 K and above), the equilibrium concentration of NO exceeds 1500 p.p.m. Considerable amounts of NO (up to 500 p.p.m.) can be formed already at 1500 K.

2. Fast nitrogen oxides

Fast nitrogen oxides are formed in the combustion of hydrocarbons as a result of the interaction of hydrocarbon radicals with atmospheric nitrogen. These processes take place mainly in the presence of a deficiency of oxygen[1,2,4]:

$$N_2+HC\rightarrow HCN+N,$$
$$N+OH\rightarrow H+NO,$$
$$HCN+(H, OH)\rightarrow CN+(H_2, H_2O),$$
$$CN+O_2\rightarrow CO+NO,$$
$$CN+OH\rightarrow CO+NH,$$
$$NH+OH\rightarrow NO+H_2,$$
$$NH+NO\rightarrow N_2+OH.$$

3. Fuel nitrogen oxides

Nitrogen-containing compounds entering into the composition of fuels (including basic compounds—derivatives of pyridine, quinoline and acridine, and neutral compounds—various amides, nitriles, derivatives of pyrrole, indole, and carbazole, and other compounds[5]) are also sources leading to the formation of nitrogen oxides.

The formation of NO_x from fuel nitrogen proceeds via a series of intermediates; in particular, in the oxidation of pyridine and pyrrole, cyclic nitriles and CO are formed as intermediates[6]. One of the intermediates is hydrogen cyanide whose formation has been noted in the pyrolysis of pyridine[7] and in the oxidation of various nitrogen-containing compounds in mixtures with fuel in the presence of a deficiency of oxygen.[8,9] Regardless of the nature of the nitrogen-containing additive (NO, NH_3, CH_3CN, pyridine), bound nitrogen is almost fully converted into HCN in the reaction zone of the flame. On moving away from the reaction zone, the amount of HCN diminishes as a result of its conversion into N_2 and NO_x. Ammonia may also be detected together with N_2, HCN, and NO_x in the products of the combustion of nitrogen-containing fuels in the presence of a deficiency of nitrogen[10].

The mechanism of the interconversion of nitrogen-containing compounds in the flame has been considered in a number of studies[9,10–13]. The following mechanism for the conversion of fuel nitrogen has been proposed:

$$\boxed{\text{Fuel nitrogen}} \rightarrow \text{HCN} \rightarrow \text{NH}_x \begin{cases} \rightarrow \text{NO}_x, \\ \rightarrow \text{N}_2 . \end{cases}$$

According to experimental data, the conversion of fuel nitrogen into HCN is rapid and the rate-limiting stage is the oxidation of HCN [13]. The degree of conversion of fuel nitrogen into oxides in flame combustion is 20–50% and above[14–16]; the yield of NO_x is influenced by the content of nitrogen in the fuel (N_f) [14–16], the coefficient of the excess of air α† [17–19], and, to a lesser extent, the combustion temperature[20].

4. Methods for the suppression of the formation of NO_x in flame combustion

In order to combust the waste products comprising thermal nitrogen oxides, methods promoting a decrease in temperature in the combustion zone are employed: recirculation of the combustion products supplied to the combustion chamber, injection of water or steam into the combustion chamber, reduction of the additional heating of air[2,21,22]. These measures are insufficiently effective for the suppression of the formation of fuel NO_x whose sensitivity to temperature is low. The principal methods for the reduction of the amount of fuel NO_x waste involved a decrease in the coefficient of the excess of air and stepwise (two-stage) combustion[23]. In the latter method, air is supplied into the primary combustion zone in an amount less than that required theoretically. This results in a decrease in the O_2 concentration and in the flame temperature and hence in a decrease in the formation of both fuel and thermal NO_x. An amount of air insufficient for the combustion of uncombusted components is introduced to the secondary zone. The temperature in the secondary zone does not then reach the level sufficient for the formation of appreciable amounts of NO_x.

The improvement of the technology of flame combustion and design and technical measures make it possible to reduce somewhat the amount of waste comprising nitrogen oxides from combustion devices, but these possibilities are limited. Furthermore, the application of methods for the suppression of the formation of NO_x such as the recirculation of the combustion products, multistage combustion, and a decrease in the coefficient of the excess of air usually lead to an increase in the content of carbon monoxide, soot, and carcinogenic substances in the effluent gases and also to a breakdown in the stability of the combustion.[24,25] The principal methods for reducing the amount of NO_x waste have been described[21] (Fig. 1).

Norms for the content of NO_x in air have been established in our country[26] and standards are being developed for the maximum permissible amounts of waste (MPW) comprising NO_x for individual undertakings and industrial complexes.[2,27] The requirements for the maximum permissible amounts of waste NO_x have already been established in a number of countries[28,29]. Thus in Japan the NO_x MPW is 60 p.p.m. for large gas-operated boilers, 150 p.p.m. for masout-operated boilers, and 200 p.p.m. for carbon dust-operated boilers[29]. The existing methods for suppressing the formation of NO_x in the flame combustion of fuels cannot ensure the fulfillment of such rigorous requirements as regards the purity of smoke gases and it is therefore necessary to resort to expensive measures such as the catalytic elimination of NO_x from gases[30]. The best results have been obtained in the catalytic reduction of nitrogen oxides by ammonia and this method has been widely adopted in recent years in industrial boiler aggregates in a number of countries.

III. Selective catalytic reduction of nitrogen oxides by ammonia

1. Principles of the method

In contrast to the methods involving the improvement of the technology of flame combustion, the processes in which smoke gases are purified ensure a much greater reduction in the amount of NO_x waste—by 60–90%. The methods for the elimination of NO_x from smoke gases[21,31–33] have come to be divided into "wet" and "dry" (Fig. 1). The wet methods, based on the absorption of nitrogen oxides by aqueous solutions of various compounds, have not found extensive application, since under these conditions there arises, firstly, the problem of the utilisation of the waste water, and, secondly, it becomes necessary to heat the gases after purification before ejection into the smoke tube, which requires a large comsumption of fuel. Among the dry methods, the reduction of NO_x to molecular nitrogen, which need not be utilised, are of greatest interest for practical employment[32].

The non-selective reduction of nitric oxide by natural gas, hydrogen, or carbon monoxide occurs at 520–670 K in the presence of catalysts[2]:

$$4NO+CH_4 \rightarrow 2N_2+CO_2+2H_2O, \quad (4)$$

$$2NO+2H_2 \rightarrow N_2+2H_2O, \quad (5)$$

$$2NO+2CO \rightarrow N_2+2CO_2. \quad (6)$$

† The coefficient of the excess of air α is defined as the ratio of the amount of air supplied for the combustion of the fuel to the amount of air required theoretically for the combustion of the given mass of fuel.

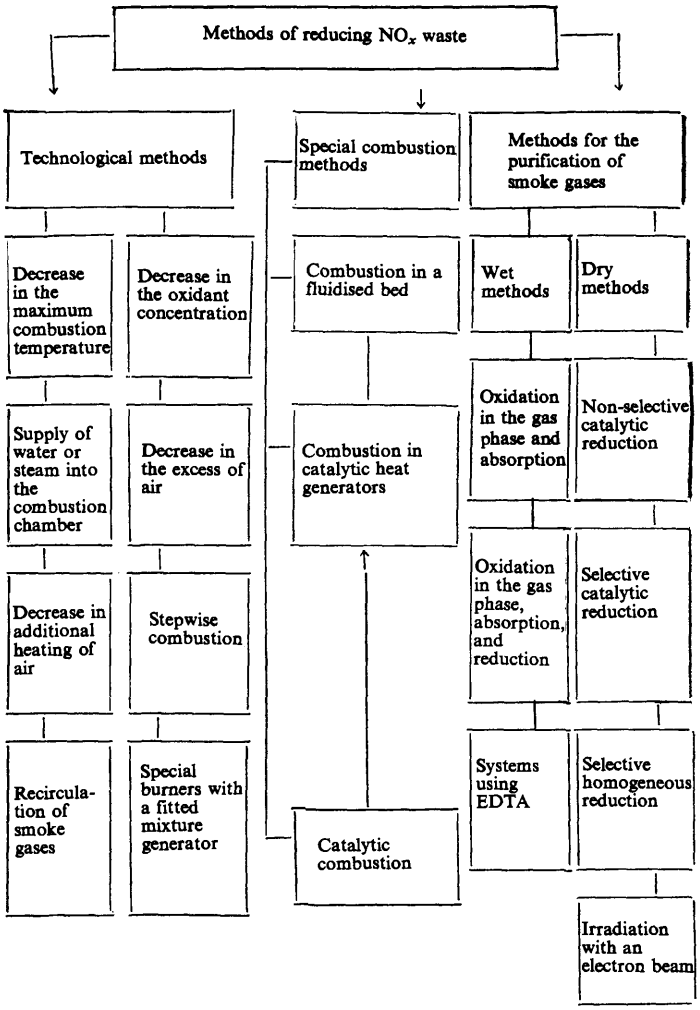


Figure 1. Methods for the reduction of NO_x waste[21].

These processes occur in a medium which contains virtually no oxygen and the first stage of the non-selective catalytic purification is therefore the "burning-off" of the oxygen in the smoke gases by the excess reductant. This consumes an amount of reductant tens of times greater than that consumed in the reaction with nitrogen oxides and methods for the non-selective catalytic reduction have not therefore found applications for the purification of smoke gases from boilers and their employment is limited to the purification of residual gases from plants for the manufacture of nitric acid[31].

The catalytic reduction of NO_x by ammonia with formation of nitrogen and water is at present regarded as the most promising of the catalytic procedures for the purification of smoke gases. This is associated with the fact that, in contrast to other reductants (methane, hydrogen, carbon monoxide, and hydrocarbons), ammonia is capable of reducing selectively nitrogen oxides in the presence of an excess of oxygen in the smoke gases[31].

The method for the selective catalytic reduction (SCR) makes it possible to reduce the amount of NO_x waste in the ideal case by more than 90%, although in practice, owing to the limitations imposed by the volume of the catalytic reactor and the permissible breakthrough of ammonia, a degree of purification of 65–80% is usually attained[32,33].

In the absence of oxygen, the interaction between ammonia and nitric oxide is described by the equation

$$4NH_3+6NO\rightarrow 5N_2+6H_2O. \quad (7)$$

In the presence of oxygen, the reduction of nitric oxide is accelerated[32] and the reaction

$$4NH_3+4NO+O_2\rightarrow 4N_2+6H_2O, \quad (8)$$

takes place. The role of oxygen consists in the reoxidation of the catalyst surface, which is converted into the reduced form following the adsorption of ammonia[31,32]. There exist data[34,35] showing that the rate of reaction of nitrogen dioxide with ammonia is independent of the oxygen concentration. The reaction proceeds in accordance with the equation

$$3NO_2+4NH_3\rightarrow 3{,}5N_2+6H_2O. \quad (9)$$

In an equimolar $NO-NO_2$ mixture, nitrogen oxides are reduced via the reaction[36]

$$NO_2+NO+2NH_3\rightarrow 2N_2+3H_2O. \quad (10)$$

Reaction (10) is the fastest of those occurring in the $NO_x-O_2-NH_3$ system[34].

Reaction (8) plays the main role in the SCR process, because in most smoke gases 90–95% of nitrogen oxides consists of NO. According to the stoichiometry of reactions (8) and (10), the molar ratio of NO_x and NH_3 should be close to unity. It has been stated[32] that a decrease in the amount of NO_x waste by 60–85% requires that the NH_3:NO molar ratio should be 0.6–0.9 and that the residual ammonia in the effluent smoke gases should be less than 1–5 p.p.m. The temperature necessary to reduce NO_x depends on the type of catalyst and is usually 570–670 K. In order to attain such temperatures without additional heating of the smoke gases, the SCR reactor is as a rule placed between the economiser and the air heater.

In the practical organisation of the elimination of NO_x from gases, it is necessary to take into account all the possible processes which may occur in the system containing the catalyst, ammonia, and smoke gases.

In the presence of oxygen, the ammonia oxidation reactions take place on the catalyst[36]:

$$2NH_3+1.5O_2\rightarrow N_2+3H_2O, \quad (11)$$

$$2NH_3+2O_2\rightarrow N_2O+3H_2O, \quad (12)$$

$$2NH_3+2.5O_2\rightarrow 2NO+3H_2O. \quad (13)$$

Reaction (13), whose occurrence can lead to an increase in the NO concentration compared with its concentration in the initial gas, is especially undesirable. Furthermore, the majority of the catalysts used accelerate the reaction[37]

$$2SO_2+O_2\rightarrow 2SO_3. \quad (14)$$

Following the breakthrough of ammonia and in the presence of SO_3 in the smoke gases, the following reactions can occur:

$$NH_3+H_2O+SO_3\rightarrow NH_4HSO_4, \quad (15)$$

$$2NH_3+H_2O+SO_3\rightarrow (NH_4)_2SO_4. \quad (16)$$

Ammonium sulphate and hydrogen sulphate are formed in these processes. A decrease in the temperature of smoke gases can lead to the contamination by the latter of the heating surfaces or of the catalyst itself. There is a possibility of a version in which the catalytic reactor is placed beyond the apparatus for the desulphurisation of the smoke gases, but in this case the latter must be heated additionally (approximately from 340 to 620 K) by combusting the gas or masout[37], i.e. as a result of an additional consumption of fuel.

Thus the most important requirements which must be met by the SCR catalysts are their high activity in the temperature range 570–670 K and their high selectivity, excluding the appreciable occurrence of the undesirable reactions (11)–(16). The requirements include[38] high resistance to erosion by the ash formed on combustion of the solid fuel, resistance to catalytic poisons present in the ash, the optimum porous structure excluding the blocking of the catalyst pores by dust, and a low hydraulic resistance.

2. Catalysts for selective catalytic reduction

SCR catalysts containing titanium, tungsten, tin, manganese, nickel[39], vanadium, molybdenum, tantalum, boron[40], chromium, iron, copper, cobalt, lanthanide[41], and uranium[42] oxides, platinum metals[43,44], cerium, iron, and manganese halides[45], transition metal ferrites[46], transition metal salts formed by the Si–W, Si–Mo, P–W, and P–Mo heteropolyacids[47], transition metal carbides[48], copper alloys[49], intermetallic compounds of platinum group metals with aluminium, scandium, titanium, and other metals[50], and zeolites[51,52] have been patented as SCR catalysts.

The catalyst carriers employed are aluminium oxide[53,54], aluminosilicates[55,56], alumina, silica[57], calcium silicate[58], titanium dioxide[59,60], a mixture of titanium dioxide and silicon dioxide[61], and zeolites[62,63]. Carriers consisting of sheet metal[64], metallic mesh[65], and ceramic honeycomb blocks[54,66,67] have been patented.

Analysis of the patent literature shows that the principal component of the catalyst carriers used to ensure the safety of the smoke gases from thermal electric power stations is titanium dioxide, which is highly stable as regards the sulphur oxides present in the smoke gases. Titanium dioxide is used both in a pure form[59,60] and together with other oxide additives: SiO_2 [61], WO_3 [68,69], MoO_3 [69], various SiO_2, Al_2O_3, ZrO_2, or ThO_2 compositions[67], as well as clay substances of the type of kaolin, montmorillonite, halloysite, pyrophyllite, or their mixtures[70]. Compounds of vanadium (V_2O_5 [59,62,63], $VOSO_4$ [71], or vanadium oxides with added TiO_2 or other metal oxides), niobium[67], silicon or zirconium[72], tungsten or molybdenum[73,74], the lanthanides[75,76], and tin[74,77,78] are usually employed as the active components of industrial catalysts. The oxides of elements in the following combinations can also serve as active components: Mn and Sn, Mn and Cd, Fe and Ni, Fe and Bi, Cr and Ni, Cr and Sb, Cu and Mo, and Co and Pb[79]. Other combinations of metal oxides, chosen from the following groups have also been proposed: Cu, Mn and Cr, on the one hand, and V, Mo, Cl, and Sn, on the other[80]. Group VB, VIB, VIIB, and VIII metal oxides are also active SCR catalysts[81].

Noble metals exhibit a high activity at 370–470 K, but their use is limited by the reduction of NO_x in the pure gases, in which there are no catalytic poisons, especially SO_2 [82]. Platinum can be employed in the range 440–520 K: the lower limit is determined by the possibility of the deposition of explosive ammonium nitrite and nitrate and the upper is set by the reaction involving the oxidation of ammonia to nitrogen oxides.

The activity of metals (deposited on Al_2O_3) diminishes in the sequence Pt $\simeq$ Pd $\gg$ Ru > Ni for the $NO-NH_3$ system, Pt $\gg$ Pd $\gg$ Ru > Ni for the $NO-NH_3-O_2$ system, Ru $\gg$ Pt, Pd, Ni for the $NO-NH_3-SO_2$ system, and Pt $\gg$ Pd, Ru > Ni for the $NO-NH_3-SO_2-O_2$ system[83,84].

In the absence of SO_2, oxygen accelerates the reduction of NO_x on platinum, ruthenium, and nickel catalysts but lowers the rate of reaction on the palladium catalyst, which can be explained by the reversible oxidation of the metal surface. In the presence of SO_2, the metal surface is covered by a monolayer of S^{2-} ions and the activity falls by 3–5 orders of magnitude; the ruthenium catalyst, whose activity falls only by a factor of 4, exhibits a notable resistance to poisoning by sulphur. The addition of oxygen to this system leads to the partial restoration of activity. Noble metals promote the ammonia oxidation side reactions in the presence of oxygen, the main one being the N_2O formation reaction (12) [83].

The activity of substituted type Y zeolites containing transition metals varies in the sequence $Pt^{II}-Y > Fe^{III}-Y > Ni^{II}-Y > Co^{II}-Y$ [85]. The zeolites are active in the temperature range 370–470 K. The presence of oxygen increases the rate of reduction of NO_x. Sulphur dioxide lowers the degree of conversion at T > 530 K, inducing the partial decomposition of the zeolite with formation of sulphates, in particular $(NH_4)_3Al(SO_4)_3$. Their deactivation in the presence of water vapour is a significant disadvantage of zeolites[86].

The activity of transition metal oxides increases in the sequence Ni < Ti, Sn, Co, Zn < W < Mo < Cr < V, Fe, Cu, Mn [31,87]. The oxides are also poisoned by sulphur, iron and vanadium oxides being the most stable. Apart from oxides, transition metal salts are active in SCR reactions: in terms of their influence on the relative catalytic activities of catalysts containing copper or iron, the counterions can be arranged in the sequence $Br^- > Cl^- > SO_4^{2-} > O^{2-}$ [88]. In the conformity with this, copper and iron oxide are less active in the absence of SO_2 than the sulphates; on the other hand, in the presence of SO_2, the oxides are converted into sulphates and their activities become similar. The activities of metal oxides in the presence of SO_2 diminish in the sequence $CuO > Fe_2O_3 > Co_3O_4 >$ NiO, while water vapour has hardly any influence[87]. Under industrial conditions, the majority of oxide catalysts, including even the most active and sulphur-resistant iron and iron-chromium catalysts deposited on alumina, lose their activity after working for several hundreds of hours as a result of poisoning by sulphur. The industrial application of the SCR method has become possible only as a result of the development of TiO_2-based catalysts, which possess a high activity and resistance to poisoning by sulphur over a wide temperature range (470–720 K) [89].

Industrial SCR catalysts usually consist of TiO_2 and a second component chosen from the oxides V_2O_5, MoO_3, WO_3, Fe_2O_3, CoO, NiO, MnO_2, Cr_2O_3, CuO, etc. Catalysts comprising TiO_2 and semiconducting *n*-type oxides (V_2O_5, $Mn_2O_3.Fe_2O_3$) are the most active in the reaction $NO+NH_3\rightarrow N_2+H_2O$, while the most active catalysts in the NO_2 reduction reaction are those based on TiO_2 and *p*-type semiconducting oxides (CoO, NiO). The anionic vacancies in the catalysts of the first type apparently promote the adsorption of

NO, while the cationic vacancies in catalysts of the second type favour the adsorption of NO_2.

It may be that TiO_2 plays the role of not only the carrier but also of a promoting agent, since the activity of mixed catalysts based on TiO_2 is higher than that of the individual oxides forming part of their composition[89].

The activity of the TiO_2-based catalysts hardly changes over a period of 2000 h and their useful lifetime during industrial employment has been estimated as 5 years. The SCR reactions on various catalysts containing the Fe, Cr, Cu, Al, Ti, and Mg oxides have been studied[89]. The $Fe_2(SO_4)_3-\alpha$-$Fe_2O_3-TiO_2$ catalyst is one of the most active both in the presence and absence of SO_x. The addition of MoO_3 or WO_3 to this catalyst increases its resistance to poisoning by sulphur and the selectivity of the reduction of NO.[89] The study of the reaction of NO with NH_3 in the presence of O_2 on V_2O_5/TiO_2 and V_2O_5/Al_2O_3 shows that the first of these catalysts is more active than the second[90]. This has been explained by the greater number of V=O surface groups participating in the reaction on the catalyst deposited on TiO_2.

3. Kinetics and mechanism of the selective catalytic reduction reactions

Reviews of studies on the kinetics of the reduction of NO by ammonia have been published[31,32,91]. On platinum, the observed reaction order with respect to NH_3 is close to unity, while the order with respect to NO is 0–0.5 [31]. Apart from nitrogen, N_2O is formed during the reaction. The mechanism of the reaction on platinum has been established with the aid of labelled nitrogen ^{15}N incorporated in the composition of NO and NH_3 [92]:

$$NH_3 \rightleftarrows NH_3(ads.),$$
$$NH_3(ads.) \rightleftarrows NH_2(ads.) + H(ads.),$$
$$NO \rightleftarrows NO(ads.),$$
$$NO(ads.) + NH_2(ads.) \rightarrow [\text{surface complex (I)}] \rightarrow N_2 + H_2O,$$
$$\vdots \quad \ldots\ldots\ldots\ldots \rightarrow N_2O + 2H(ads.),$$
$$H(ads.) + NO(ads.) \rightarrow HNO(ads.),$$
$$2HNO(ads.) \rightarrow [\text{surface complex (II)}] \rightarrow N_2O + H_2O,$$
$$\vdots \quad + 2H(ads.) \rightarrow N_2 + 2H_2O.$$

The rate of the reaction of NH_3 with NO on copper-containing zeolites is described by the kinetic equation[86]

$$w = \frac{kK_{NO}K_{NH_3}p_{NO}p_{NH_3}}{(1 + K_{NH_3}p_{NH_3} + K_{H_2O}p_{H_2O})^2},$$

where k is the rate constant for the reaction of the adsorbed NH_3 and NO, K_i the equilibrium constant for the adsorption of the corresponding components of the reaction mixture, and p_i are the corresponding partial pressures. This equation corresponds to the mechanism in which the rate-limiting stage is the interaction of the strongly adsorbed NH_3 with the weakly coordinated NO. The equation indicates the cause of the inhibition of the reaction by water: water displaces ammonia, competing with it for the surface centres.

The following mechanism has been postulated for the SCR reaction on copper oxide and copper sulphate catalysts[87]:

$$NO \rightleftarrows NO(ads.),$$
$$NH_3 \rightleftarrows NH_2(ads.) + H(ads.),$$
$$O_2 \rightleftarrows 2O(ads.),$$
$$2H(ads.) + O(ads.) \rightleftarrows H_2O,$$
$$NO(ads.) + NH_2(ads.) \rightleftarrows N_2 + H_2O.$$

According to this mechanism, the overall rate of the process is determined by the rate of the stage involving the reaction of the adsorbed NO with the dissociatively adsorbed NH_3.

In a study[91] of the kinetics of the reaction of NO with NH_3 on the $V_2O_5/SiO_2.TiO_2$ industrial catalysts, the rate of the process was fitted by the kinetic equation $w = kc_{NO}^{n_1}c_{NH_3}^{n_2}c_{O_2}^{n_3}$. At temperatures in the range 550–650 K, the reaction orders are 0.7–0.8 with respect to NO, 0.1–0.3 with respect to NH_3, and 0.1–0.3 with respect to oxygen. Internal diffusion conditions occur in this temperature range and the activation energy is 28 kJ mol^{-1}. The mechanism of the reaction on V_2O_5 proposed by Miamoto et al.[90] relates the activity of the catalyst to the concentration of the surface V=O groups:

$$V{=}O + NH_3 + NO \rightarrow V{-}OH + N_2 + H_2O,$$
$$3V{=}O + 2NH_3 \rightarrow 3V\square + N_2 + 3H_2O,$$
$$V\square + 0.5O_2 \rightarrow V{=}O,$$
$$V\square + NO \rightarrow V{=}O + 0.5N_2,$$

where V□ is a V–OH group or an oxygen vacancy on the surface. In contrast to this, it has been shown[93] that N_2 is formed predominantly on the single crystal faces coated by hydroxy-groups and that there is a correlation between the number of adsorbed NH_4^+ ions and the amount of N_2 formed. The following mechanism is consistent with similar ideas:

$$V^{5+}{-}OH + NH_3 \rightarrow V^{5+}{-}ONH_4,$$
$$2V^{5+}{-}ONH_4 + V^{5+}{-}O{-}V^{5+} + 2NO \rightarrow$$
$$2N_2 + 3H_2O + V^{5+}OH + V^{4+}\square V^{4+},$$
$$V^{4+}\square V^{4+} + 0.5O_2 \rightarrow V^{5+}{-}O{-}V^{5+},$$

where □ is an oxygen vacancy on the surface.

4. Industrial use of selective catalytic reduction

In order to eliminate NO_x from smoke gases with a high content of SO_x and solid particles, mainly only two types of block catalysts are employed in industry: lamellar catalysts made from cast metal plates and monolithic catalysts with a ceramic honeycomb structure.

The lamellar catalysts developed by the Hitachi company (Japan) consist of steel sheets plated by the plasma sputtering of stainless steel with subsequent deposition of the catalytic mass. The catalyst plates, the gap between which is 5–6 mm, are assembled into 450 × 450 × 500 mm blocks. Jointly assembled 10–20 blocks comprise catalyst modules weighing from 1.11 to 2.02 tonnes.

The reduction temperature is 570–690 K. Depending on the temperature of the gases and their content of SO_x and ash, different modifications of the catalysts are employed[94].

Different types of honeycomb catalysts on a ceramic base have been developed by the Mitsubishi and Sakai companies (Japan). Depending on the type of fuel, different ratios of the active substances—titanium dioxide, tungsten trioxide, and vanadium pentoxide—are used. The catalysts are made in the form of rectangular blocks 500–1000 mm long and with a 150 × 150 mm cross-section. In each block there are 20 × 20 or 33 × 33 honeycomb cells; the longitudinal cross-sections through the honeycomb cells range from 3.5 × 3.5 to 6 × 6 mm. The surface of the catalyst varies from 430 to 678 m^2 per m^3 of its volume. The catalysts are assembled into modules containing between 36 and 100 blocks[95].

The SCR method has found the most extensive application in Japan, where 20 devices, fitted on large carbon dust energy units, began to operate in 1980–1986. In addition, towards the end of 1985, a further 200 devices for the catalytic purification of smoke gases operated in Japan on thermal electric power station boilers with an overall power of 30 GW[33].

Industrial SCR devices are being introduced in the Federal Republic of Germany[96], Australia[97], and West Berlin[98]. Experimental studies on SCR are being prosecuted in Sweden[99].

The experience gained in the use of industrial SCR devices has shown that the guaranteed useful lifetime of the catalysts is between 1 and 2 years. In fact, the average useful lifetime reaches 5 years in the combustion of liquid fuel and 7 years in the combustion of gas[100]. In order to prolong the useful lifetime of the catalyst, it is essential to free the gases from dust, which erodes the active surface. However, fine dust particles, which are difficult to remove, can block the pores of the catalyst, which also reduces its useful lifetime[100].

Each MW of the measured power of the energy unit usually requires 2 m^3 of the catalyst, costing 30000 German marks (10000 roubles) per m^3[101].

The specific cost of the purification of smoke gases using the SCR method depends comparatively little on the power of the plant and varies from 106 to 222 German marks per kilowatt (40–80 roubles/kW) for energy units with power ranging from 150 to 700 MW. The cost of the catalyst itself is then 40% of the overall cost of the apparatus[33].

The requirements which must be met by the catalysts in the purification of gases by the SCR method are more stringent than in the catalytic combustion of fuels. In many cases, especially in the generation of heat for domestic purposes or for various technological processes, ecologically pure catalytic combustion can compete with flame combustion combined with purification of smoke gases.

IV. Catalytic combustion as a method of preventing the formation of nitrogen oxides

1. Principles of catalytic combustion

The catalytic combustion of fuels is a special case of total oxidation. The specific features of catalytic combustion consist in the fact that the catalyst should ensure the complete combustion of highly concentrated mixtures of hydrocarbons under conditions where the ratios of the reaction components are close to the stoichiometric ratios and when a large amount of heat is evolved. The total oxidation catalyst can therefore be used, in principle, also for catalytic combustion. However, these catalysts must exhibit an improved heat resistance, stability, and resistance to catalytic poisons which may be present in the fuel. The history of the problem and the principles governing the selection of catalysts have already been examined in detail[102–109]. The principal results of the latest studies on the catalytic combustion of fuels have been described in reviews[108–112].

Studies on the use of catalytic combustion for domestic, energy generating, and technological requirements are developing in several directions. Small catalytic heat sources for the heating of domestic and industrial accommodation and means of transportation are being created[113–124]. Extensive studies are being prosecuted on the catalytic combustion in the combustion chambers of gas turbines[125–134]. The catalytic combustion of gases with a low heat of combustion and a low temperature of the effluent gases in a number of industrial undertakings is believed to be extremely promising[135]. In all the devices listed, the fuels are combusted in a stationary catalyst bed consisting of noble metals deposited on fibrous and block carriers at temperatures in the range 1100–1600 K.

The principal advantage of the catalytic combustion of fuels is believed by the majority of workers to be the possibility of a significant decrease in the amount of harmful waste[131,132]. Indeed, the use of a catalyst makes it possible to increase the degree of conversion of the hydrocarbon fuel and to eliminate the formation of CO and of carcinogenic hydrocarbons usually formed in flame combustion. In the catalytic combustion of fuels which do not contain bound nitrogen in gas turbines at 1200–1500 K, the concentration of NO_x in the effluent gases diminishes from 150 to 2 p.p.m.[129,130] In model boiler plants with catalytic combustion of a gaseous fuel at 1400–1600 K, a tenfold decrease in the amount of NO_x waste (from 150 to 15 p.p.m.) is achieved[130]. The advances made concern principally pure fuels (petroleum gas and petroleum distillates) and arise from the fact that the decrease in temperature makes it possible to rule out completely the formation of high-temperature "thermal" nitrogen oxides. At the same time the problem of reducing the amount of waste "fuel" nitrogen oxides in working experimental devices has apparently not yet been solved. Thus, in the combustion of nitrogen-containing fuels, an almost complete conversion of the nitrogen of the fuel into nitrogen oxides has been observed in the catalytic chamber of the gas turbine[130]. Other difficulties and limitations accompanying the employment of devices with a stationary catalyst bed in the form of honeycomb structures or other blocks have also been discovered. The catalytic combustion is accompanied by extensive adiabatic heating, as a consequence of which the catalyst blocks must possess a series of unique properties. On the one hand, they must have a minimal wall thickness and must be characterised by a minimal hydraulic resistance and, on the other hand, they should exhibit the maximum stability as regards large temperature drops during prolonged use. The employment of platinum group metals as the active component leads to an appreciable increase in the cost of the catalytic devices. Platinum and palladium may be poisoned by catalytic poisons and are suitable only for the combustion of fuel free from such poisons[135]. The devices described are not suitable for the combustion of liquid fuels obtained by the hydrogenation of coal or masout, since they contain catalytic poisons and cannot be fully vaporised to be supplied into the catalytic chamber in the vapour phase.

Catalytic heat generators (CHG) for the combustion of fuel have been developed by the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[103,111,136–138]. The combustion of

fuels in CHG is based on four principles: (1) the use of total oxidation catalysts; (2) the use of a fluidised bed of catalyst particles; (3) the combustion of nearly stoichiometric fuel–air mixtures; (4) the combination of heat evolution and heat removal in a single catalyst bed.

Thus the non-flame combustion of fuels in CHG takes place on the surface of catalyst particles in a fluidised state. Like any fluidised bed apparatus, the CHG consists of a hollow vessel in the lower section of which there is an air distributing grid. Fluidisation occurs during the ascending movement of a mixture of air with the fuel as well as the combustion products through the bed of spherical catalyst particles. The useful removal of heat from the CHG is achieved either through the surface of a heat exchanger in contact with the fluidised catalyst bed or via a working body in direct contact with the catalyst. The fundamental advantage distinguishing the CHG from the devices described in the literature for the combustion of fuels in a fluidised catalyst bed[139–145] is the presence of a horizontal sectioning grid with a specified live section and a rigorously specified diameter of the apertures. This results in the creation of two zones of a free fluidised bed—below the sectioning grid and above it. The height of the lower zone should be such that complete oxidation of the fuel is ensured. The sectioning grid limits the circulation of the catalyst particles and hence the thermal conductivity of the bed. It plays the role of a non-isothermal packing and divides the apparatus along its height into two isothermal zones: the lower zone whose temperature is necessary for the complete oxidation of the fuel (700–1000 K) and the upper zone whose temperature is determined by the conditions in the heating of the working body[111,146,147] (Fig. 2). The presence of the non-isothermal packing and the removal of heat from the upper part of the apparatus make it possible to reduce the temperature of the effluent gases to 420–450 K.

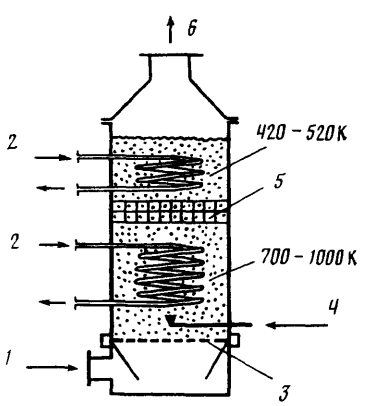


Figure 2. Schematic illustration of a non-isothermal catalytic heat generator[111]: *1*, air; *2*, water; *3*, gas distributing grid; *4*, fuel; *5*, non-isothermal head-piece; *6*, effluent gases.

Analysis showed that catalytic combustion makes it possible to solve the ecological problems arising in the use of the so called "pure fuels" without bound nitrogen. Unfortunately the fraction of such fuels with diminish as the trends which have arisen towards the employment of coal, masout, and coal liquefaction products intensify. Such fuels contain bound nitrogen which can form during catalytic combustion an amount of nitrogen oxides which is not less than in flame combustion. The specific features of the extensive oxidation reactions of nitrogen-containing compounds consist in the fact that both molecular nitrogen and nitrogen oxides can be formed from them:

$$RN + O_2 \rightarrow CO_2 + H_2O + N_2, \quad (17)$$

$$RN + O_2 \rightarrow CO_2 + H_2O + NO_x. \quad (18)$$

In catalytic combustion processes, it is important to achieve a decrease in the yield of fuel NO_x via reaction (18) as a result of the preferential occurrence of reaction (17). To solve this problem, it is essential to investigate the kinetics and mechanism of the catalytic oxidation of nitrogen-containing compounds of different classes.

2. Kinetics and mechanism of the catalytic oxidation of nitrogen-containing compounds

(a) Oxidation of ammonia and hydrogen cyanide. The catalytic oxidation of ammonia has been studied in very great detail, since this reaction is one of the most important processes in heterogeneous catalysis[148,149]. It can proceed via three principal pathways described by Eqns. (11)–(13). All the reactions indicated are almost irreversible.

The present state of the theory of catalytic oxidation of ammonia has been described satisfactorily by Il'chenko[150]. By analogy with the oxidation of organic compounds, molecular nitrogen should be regarded as the product of mild oxidation, while nitrogen oxides are products of extensive oxidation. In the presence of many catalysts, three nitrogen-containing products (N_2, N_2O, NO) in various proportions are formed simultaneously at 673–773 K. On the other hand, by using selective catalysts and by carrying out the reaction under specified conditions, one can ensure the preferential occurrence of one of the processes. Thus at high temperatures (1073–1173 K) on platinum catalysts, the yield of nitrogen oxides can reach 96–99%, which is achieved in practice in the manufacture of nitric acid. The oxidation of ammonia on platinum begins at 423–473 K where the only nitrogen-containing reaction product is molecular nitrogen. With increase in temperature, N_2O appears, its yield passing through a maximum. At temperatures of the order of 573 K, the formation of nitric oxide begins. The yield of this product gradually increases and can exceed 90% at 973–1273 K [148,150].

The oxidation of ammonia on other catalysts proceeds similarly but the temperature limits in the formation of the products of mild and extensive oxidation can be different. The specific catalytic activity of metals in the oxidation process decreases in the sequence Pt > Pd > Cu > Ag > Ni > Au > Fe > W > Ti. The corresponding activity series for oxide catalysts has also been found: Co_3O_4, MnO_2 > CuO > ZnO > CaO_2 > NiO > Bi_2O_3 > Fe_2O_3 > V_2O_5 > TiO_2 > CdO > PbO > SnO_2 > ZrO_2 > MoO_3 > WO_3 [149–152]. The decrease in activity is associated with the increase in the bond energy between oxygen and the metal surface. The selectivity in the extensive oxidation (to N_2O and NO) diminishes in approximately the same sequence. The point is that, in the extensive oxidation process, a larger number of oxygen–catalyst bonds are broken that in the formation of the mild oxidation product (N_2). With increase in the bond energy between oxygen and the metal surface, the rate of extensive oxidation should therefore

diminish more rapidly than the rate of mild oxidation, which in fact leads to a change in selectivity in the series quoted above[148,149].

A similar behaviour has been observed in the study of the catalytic oxidation of hydrogen cyanide[153]. In this case, the activity and selectivity of the catalysts are also determined by the bond energy between oxygen and the catalyst surface[148].

(b) Oxidation of organic nitrogen-containing compounds. Comparatively few data on the kinetics of the extensive oxidation of organic nitrogen-containing compounds have been described in the literature. The studies carried out have been devoted mainly to the selection of conditions governing the use of catalysts for the additional combustion of the waste from different industries.

Thus the oxidation of dimethylformamide has been studied on the AVK-10 (10% V_2O_5/Al_2O_3), NIIOGAZ-7D ($Cr_2O_3+CuO+V_2O_5$), ShPK (0.2% Pt/Al_2O_3), and AP-56 (0.5% Pt/Al_2O_3) industrial catalysts at 573–623 K [154]. The formation of nitrogen oxides at concentrations up to 18 p.p.m. has been observed on platinum catalysts. On oxide catalysts, NO_x were either not formed or were evolved in trace amounts.

The kinetics of the oxidation of dimethylacetamide in the presence of the NIIOGAZ-7D catalyst were investigated on a flow-circulation apparatus in the temperature range 503–653 K [155]. The amount of nitrogen oxides formed increased with increase in the initial dimethylacetamide concentration and temperature.

The possibility of making safe the dimethylamine-containing waste water by the vapour phase catalytic oxidation of dimethylamine has been studied on a flow apparatus[156]. At 700–750 K and at a vapour–gas flow rate of 2000–4000 h^{-1}, the GIPKh-105 catalyst ensured 94% conversion of dimethylamine via the reaction

$$4(CH_3)_2NH+15O_2\rightarrow 2N_2+8CO_2+14H_2O.$$

The formation of nitrogen oxides in the catalytic oxidation of ammonia and ethylenediamine has been investigated in flow apparatus on AP-56, NTK-1 (53% ZnO, 24% Cr_2O_3, and 12% CuO) and GIPKh-105 (40% CuO and 40% Cr_2O_3) catalysts[157], whose efficiency was estimated from the degrees of conversion of the compounds indicated in extensive oxidation reactions. The GIPKh-105 catalyst, ensuring 100% conversion of both ethylenediamine and ammonia at 573 K, a 15000 h^{-1} space velocity, and a concentration of 10 mg $litre^{-1}$ proved to be best. In the oxidation of ammonia (c = 15 mg $litre^{-1}$) the degree of conversion of the bound nitrogen into oxides was 3% at 623 K, while the degree of conversion in the oxidation of ethylenediamine (c = 6.8 mg $litre^{-1}$) was 38%. On reducing the temperature to 473 K, the concentration of NO_x diminishes severalfold. In the joint presence of ethylenediamine and ammonia, the yield of nitrogen oxides is appreciably lower than in their separate oxidation. The authors believe[157] that one of the stages involved the reaction of nitric oxide, formed in the oxidation of ethylenediamine, with the ammonia present in the gas mixture in accordance with the scheme

$$NO(ads.)+NH_3(ads.)+O(ads.)\rightarrow N_2+H_2O+OH(ads.).$$

As a result of this, the yield of nitrogen oxides in the oxidation of a mixture of ethylenediamine and ammonia is significantly reduced. The complete elimination of pyridine from the waste in chemopharmaceutical industries is achieved on aluminoplatinum, copper–chromium, copper–manganese, and aluminocopper catalysts at a temperature of about 623 K [158–160]. The selectivity with respect to N_2 is 85–92% [159].

The extensive aniline oxidation reaction in the presence of the aluminoplatinum catalyst has been studied in greatest detail[161,162]. The experiments were performed in a flow-circulation apparatus at an initial aniline concentration of (0.5–240) × 10^{-6} M and at space velocities of the stream of 250–10000 h^{-1}. The rate of oxidation of aniline obeys the equation

$$w = k\frac{c_A c_{O_2}^{0.5}}{1+k'c_A},$$

where c_A and c_{O_2} are the stationary concentrations of aniline and oxygen respectively, $k = 8.14\times10^{10}\,e^{-84018/RT}$ $litre^{1.5}\,mol^{0.5}\,h^{-1}\,g^{-1}$, $k' = 2.24\times10^{3}\,e^{21736/RT}$ litre mol^{-1}. The contents of nitrogen oxides in the reaction products for a degree of conversion of aniline of 0.9 and at 473, 573, and 673 K are respectively 0.2, 5.1, and 10.7% relative to the aniline which has reacted. The extensive aniline oxidation reaction has been described by a scheme incorporating twelve stages[162] of which the first five concern the reaction of bound nitrogen:

(1) $O_2\rightleftarrows 2O(ads.)$,

(2) $C_6H_5NH_2+O(ads.)\rightleftarrows C_6H_5NH_2O(ads.)$,

(3) $C_6H_5NH_2O(ads.)+O(ads.)\rightleftarrows C_6H_5NOOH_2(ads.)$,

(4) $C_6H_5NOOH_2(ads.)\rightleftarrows C_6H_5(ads.)+NO+H_2O$,

(5) $C_6H_5NH_2O(ads.)+NO\rightarrow C_6H_5O(ads.)+N_2+H_2O$.

It has been suggested that stages 1–3 virtually correspond to equilibrium, stage 4, representing the decomposition of compounds of the peroxide type, is slow, while stage 5 as well as the remaining stages not quoted here are rapid and irreversible. The following kinetic equations follow from the above scheme on the assumption of high coverages of the catalyst surface:

$$w = k_4\frac{K_1K_2K_3p_{O_2}p_A}{K_1p_{O_2}^{0.5}+K_1K_2p_{O_2}^{0.5}p_A+K_1K_2K_3p_{O_2}p_A},$$

where K_1, K_2, and K_3 are the equilibrium constants of stages 1, 2, and 3 and k_4 is the rate constant for stage 4. This equation is converted into the experimental expression when $K_1K_3 \ll 1$.[162]

The above scheme makes it possible to account for the virtually complete absence of nitrogen oxides in the oxidation of aniline on the catalyst: NO is formed slowly in stage 4 but is rapidly consumed in stage 5. Indeed, in the oxidation of aniline adsorbed on the catalyst by nitric oxide, mainly molecular nitrogen was formed. Detailed kinetic studies on the extensive catalytic oxidation reactions of a series of nitrogen-containing compounds were carried out in order to establish the principles governing the decrease in the NO_x concentration in the catalytic combustion of nitrogen-containing fuels[163–169]. The objects of study were compounds differing in the nitrogen-containing functional groups. Catalysts developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences for catalytic heat generators as well as a series of other typical total oxidation catalysts, especially industrial final combustion catalysts IK-12-1 and AK-64, were used.

In the study of the pyridine oxidation reaction[163,164,169] in the temperature range 513–820 K, the initial pyridine concentration was varied in the range 0.05–2.0 vol.% and the oxygen concentration

was varied in the range 4.2–50 vol.%. The oxidation products were CO_2, H_2O, N_2, and NO_x (NO and NO_2). In the kinetic region (at 633 K and below), the order of the extensive oxidation reaction with respect to pyridine was zero and that with respect to oxygen was close to unity on all the deposited catalysts. The NO_x formation reaction was also zero order with respect to pyridine. The kinetic parameters of the extensive oxidation reactions and the nitrogen oxide formation reactions as well as the degrees of conversion of bound nitrogen into oxides (X_{NO_x}) on certain catalysts are listed in Table 1. A significantly smaller amount of NO_x is formed on oxide catalysts than on the platinum catalyst under the same conditions. Oxide catalysts propagate the oxidation to molecular nitrogen with a high selectivity, the degree of conversion of bound nitrogen into oxides not exceeding as a rule several per cent. In the presence of the copper–chromium catalysts, the rate of formation of nitrogen oxides increases with increase in the content of copper chromite in the catalyst.

Table 1. Kinetics of the catalytic oxidation of pyridine (c_{RN} = 0.5%)[163,164,169].

Catalyst	Sample, g	Extensive oxidation		Formation of NO_x			
		10^{-10} w, mol C_5H_5N cm^{-2} s^{-1}, 573 K	E_{act}, kJ mol^{-1}	10^{-8} w, mol NO_x cm^{-2} s^{-1}, 573 K	E_{act}, kJ mol^{-1}	c_{NO_x}, p.p.m., 573 K	x_{NO_x}, %, 573 K
5% $CuCr_2O_4/\gamma$-Al_2O_3	2.18	0.5	154±26	1.3	170±26	8	2.6
11% $CuCr_2O_4/\gamma$-Al_2O_3	2.09	2.2	170±3	2.5	—	9	1.1
30% $CuCr_2O_4/\gamma$-Al_2O_3	0.29	0.8	182±12	9.0	170±6	11	11.1
28% $NiCr_2O_4/\gamma$-Al_2O_3	1.02	2.0	184±12	3.9	—	9	2.0
26% CuO/γ-Al_2O_3	1.8	4.0	170	7.1	—	27	1.8
0.64% Pt/γ-Al_2O_3	1.8	2.0	158±8	50.0	125±17	48**	25.0
γ-Al_2O_3	1.8	0.002*	221±11	—	—	1***	0.1

* Found by extrapolating the experimental data to temperatures above 623 K.
** At 543 K.
*** At 623 K.

The catalytic oxidation of acetonitrile, nitromethane, and dimethylformamide has been investigated[165,167]. Their extensive oxidation reactions were investigated in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 catalyst in the range of initial acetonitrile concentrations from 0.12 to 3.0 vol.%, nitromethane concentrations from 0.24 to 1.95 vol.%, and dimethylformamide (DMF) concentrations from 0.01 to 0.68 vol.%. The oxygen concentration in the oxidation of CH_3CN was varied from 13 to 50 vol.%, while in the oxidation of CH_3NO_2 and DMF it was always 50 vol.%. The studies were performed on flow-circulation apparatus in the temperature range 453–793 K. The principal kinetic parameters of the extensive oxidation reactions are listed in Table 2.

Above 623 K, the nitrogen-containing compounds are fully converted into oxidation products. The degree of conversion of bound nitrogen into NO_x in such a complete reaction is determined by the nature of the active component of the catalyst employed, the concentrations of the substance oxidised and oxygen in the reaction mixture, and temperature. In the oxidation of pyridine, acetonitrile, and DMF in the presence of oxide catalysts, the main bulk of the bound nitrogen is converted into N_2, while the yield of nitrogen oxides does not exceed several per cent. An appreciably higher degree of conversion of bound nitrogen into NO_x is characteristic of the platinum catalyst—up to 40% in the case of pyridine and up to 90% in the case of acetonitrile (Fig. 3). At a constant temperature and in an excess of oxygen, the quantity X_{NO_x} in the presence of all the catalysts investigated falls with increase in the initial concentration of the oxidised substance in the reaction mixture.

Table 2. Kinetics of the extensive oxidation of certain nitrogen-containing compounds in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 (c_{RN} = 0.5%) catalyst[165–167]

Compound	T, K	10^{-10} w, molecules cm^{-2} s^{-1}	E_{act}, kJ mol^{-1}	Reaction order	
				w.r.t. RN	w.r.t. O_2
Acetonitrile	573	29.0	100	0	0.9
Nitromethane	573	100	100	0	—
Dimethylformamide	513	10	53	0.5	—

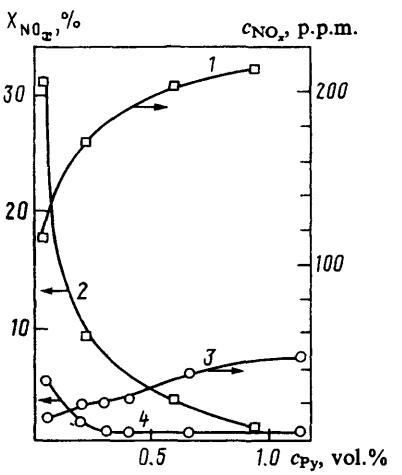


Figure 3. Dependence of the NO_x concentration (curves *1* and *3*) and of the degree of conversion of bound nitrogen into NO_x (curves *2* and *4*) on the initial pyridine concentration at 673 K in the presence of the 0.64% Pt/γ-Al_2O_3 (curves *1* and *2*) and 5% $CuCr_2O_4/\gamma$-Al_2O_3 (curves *3* and *4*) catalysts[164].

The NO_x concentration depends little on the oxygen concentration, while the coefficient of the excess of oxygen $\alpha > 1.5$ and diminishes sharply as the reaction mixture approaches the stoichiometric composition. An increase in temperature entails an increase in X_{NO_x}. For copper–chromium catalysts, the dependence of the amount of

nitrogen oxide formed and X_{NO_x} on the concentration of the active component ($CuCr_2O_4$) in the catalyst was obtained. The NO_x concentration and X_{NO_x} increase in the sequence γ-Al_2O_3 < 5% $CuCr_2O_4/\gamma$-Al_2O_3 < 11% $CuCr_2O_4/\gamma$-Al_2O_3 < 30% $CuCr_2O_4/\gamma$-Al_2O_3.

Table 3. The formation of nitrogen oxides in the complete oxidation of nitrogen-containing compounds in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 catalyst[165–167].

Compound	Catalyst sample, g	c_{RN}, vol.%	T, K	c_{NO_x}, p.p.m.	X_{NO_x}, %
Acetonitrile	0.53	1.09	623	16	0.2
	0.53	0.95	723	26	0.3
	7.04	2.45	768	159	0.7
Dimethylformamide	3.17	0.66	673	17	0.3
	3.17	0.66	723	234	3.6
Pyridine	2.28	1.09	673	122	1.1
	2.28	1.09	723	588	5.4
	15.06	0.95	793	1 336	14.4
Nitromethane	1.19	1.07	673	7 940	76.8
	6.05	1.07	758	10 220	99.2

Table 3 presents data concerning the influence of the nature of the oxidised compound on the yield of NO_x in the range of high temperatures (>620 K) in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 catalyst. The maximum amount of NO_x is formed in the oxidation of nitromethane, which is apparently associated with the presence of the NO_2 group in the molecule. On the basis of the set of kinetic relations obtained as well as literature data concerning the forms of adsorption of pyridine and the extensive oxidation of organic compounds, the following mechanism for the conversion of pyridine has been proposed[168,169]:

$$C_5H_5N \xrightarrow{k_1} C_5H_5N(ads.),$$

$$C_5H_5N(ads.) + O_2 \xrightarrow{k_2} HN-C_5H_4OO(ads.),$$

$$HNC_5H_4OO(ads.) + O_2 \xrightarrow{k_3} NH(ads.) + CO_2 + C_4H_4OO(ads.) \xrightarrow[fast]{}$$

$$\rightarrow CO_2, H_2O, N_2, NO_x.$$

In the first stage, pyridine is adsorbed on the surface, in the second stage the aromatic ring is cleaved, while in the third stage a C–N bond is ruptured with formation of surface groups. The kinetic equation which follows from the last scheme on the assumption that $k_1 p_{C_5H_5N} \gg k_2 p_{O_2}$ and $k_3 p_{O_2}$ has the form $w = k p_{O_2}$. It describes adequately the experimental data. It must be emphasised that all observations indicate the dissociation of C–N bonds in the first stages of the oxidation process. Compounds with such a bond, including HCN, were not detected in the reaction products. Furthermore, in special experiments on the oxidation of pyridine and acetonitrile under the conditions of a deficiency of oxygen, the degree of conversion of bound nitrogen into NH_3 reached 10%, while HCN was formed in trace amounts. The oxidative reactions of the type NH_x surface groups formed apparently proceed via the mechanism proposed for the ammonia oxidation reaction[148]:

(1) $NH(ads.) + O(ads.) \rightleftarrows HNO(ads.)$,

(2) $NH(ads.) + HNO(ads.) \rightleftarrows N_2 + H_2O$,

(3) $HNO(ads.) + HNO(ads.) + O(ads.) \rightleftarrows 2NO + H_2O$,

(4) $NO + O(ads.) \rightleftarrows NO_2$.

Apparently stages 1 and 2 take place preferentially on oxide catalysts, while on aluminoplatinum catalysts stages 3 and 4 also make a significant contribution, i.e. the catalysts differ in the ratio of the rate constants for the corresponding stages.

The above investigations have led to the conclusion that the possible routes to a decrease in the waste nitrogen oxides in the catalytic combustion of nitrogen-containing fuels involve the use of oxide catalysts, a decrease in temperature, and a decrease in the coefficient of the excess of air.

3. Characteristic features of the formation of fuel NO_x in the catalytic combustion fuels

A series of studies on the reactions of nitrogen in fuels during catalytic combustion have been published[130,134,170–182]. The yield of fuel NO_x is influenced by the combustion temperature, the coefficient of the excess of air α, the nitrogen content in the fuel, and the nature of the catalyst (Table 4).

It has been established[171] that in the combustion of mixtures of propane with ammonia and methylamine, the form of the nitrogen-containing additive does not affect the yield of nitrogen oxides. The degree of conversion of nitrogen into NO_x increases with increase in temperature[171,172]. Thus, in the combustion of propane with added NH_3 and CH_3NH_2, the quantity X_{NO_x} increases from 30% at 1100 K to 80% at 1400 K. A further increase in temperature to 1600 K hardly affects the increase in X_{NO_x}, which is 80–90%[171].

The dependence of the degree of conversion of the fuel nitrogen into NO_x on the coefficient of excess of air α has been studied in greatest detail. In the range $1.2 \leqslant \alpha \leqslant 2.0$, the degree of conversion of bound nitrogen into oxides depends little on α and diminishes by a factor of 2–3 as the fuel–air mixture approaches the stoichiometric composition[130,170–181]. For $\alpha \leqslant 1$, the combustion products contain ammonia and hydrogen cyanide. Under these conditions, a decrease in the amount of air leads to a further decrease in the NO_x concentration owing to the increase in the N_2, NH_3, and HCN concentrations[130,131,170]. For certain values of α, which are usually in the range 0.6–0.9, the maximum degree of conversion of bound nitrogen into N_2 is attained (up to 80–90%). It has therefore been suggested[171] that the catalytic combustion be carried out in two stages: $\alpha < 1$ is established in the first stage (usually between 0.5 and 0.9), while in the second stage an excess of air is supplied to achieve the final combustion of the uncombusted substances. On average $\alpha \geqslant 1$ for the entire process. The two-stage catalytic combustion at 1400–1500 K ensures a decrease in the degree of conversion of fuel nitrogen into oxides from 80–100% (for single-stage combustion) to 10–30%[130,172,176,177]. However, an increased deactivation of the catalyst as a consequence of its saturation by coke is then observed in the first stage[172]. A scheme for the two-stage combustion of liquid nitrogen-containing fuels using a catalyst only in the second stage has been proposed.[134]

Table 4. The formation of NO_x in the catalytic combustion of fuel (literature data).

Fuel combusted	Catalyst	Nitrogen-containing additive	N_f^*, %	T, K	α	Studied dependence of X_{NO_x} on				Refs.
						α	N_f	type of catalyst	temperature	
$CO+H_2+CH_4+N_2$ (model mixture)	2.1–6.3% Pt on a monolithic carrier with a variable cross-section of channels	NH_3	0.0471	1273	0.4–2.3	+	–	–	–	[174]
CH_4	ditto	NH_3	0.9417	1273	0.4–2.3	+	–	–	–	[174]
CH_4, C_3H_8	Pt, NiO+Pt on a monolithic carrier	NH_3 or CH_3NH_2	0.003–3.6	1100–1600	0.6–2.2	+	+	+	+	[171]
C_3H_8	0.18% Pt on monolithic cordierite ite covered with Al_2O_3	NH_3	2.0	1000	0.8–1.0	+	+	–	–	[175]
$CO+H_2+CH_4+N_2$ (model mixture)	Pt/Al_2O_3, NiO/ZrO_2	NH_3	0.05–0.24	1480	0.4–1.2	+	–	+	–	[177]
C_3H_8, CH_4	Noble metal on a monolithic carrier	NH_3	0.2	1000–1500	0.5–1.3	+	–	–	–	[130]
CH_4	Co_2O_3, NiO+Pt, Co_2O_3+Pt, Pt on a monolithic carrier	NH_3	0.2–2.0	1100–1900	0.5–2.0	+	+	–	+	[172]
CH_4	ditto	»	»	»	»	+	+	+	+	[176]
C_3H_8	5.63% $Cr_2O_3+Co_2O_3$	NH_3	1.0	1200–1300	0.5–1.8	+	–	–	+	[178]
Kerosene	0.2% Pt on a carrier with a honeycomb structure	C_5H_5N	0.3	1470–1770	0.9–1.1	+	–	–	–	[134]
Diesel fuel	2% Pt on a monolithic carrier	C_6H_5N	0.125; 0.535	1000–1700	1.0–4.0	–	+	–	–	[179]
Diesel fuel	5.3% Pt on a monolithic carrier	none	0.0135	1100–1400	1.0	Independent of conditions				[182]
Artificial liquid fuels from coal, diesel fuel	2% Pt/Al_2O_3, 2% Pt on a monolithic carrier	none	0.31–0.86	1370–1530	0.7–1.7	+	–	–	–	[180]
Diesel fuel	Noble metal on a monolithic carrier	C_5H_5N	0.5	1000–1500	2.0–3.5	+	–	–	–	[181]
Masout	Monolithic catalyst with a variable cross-section of channels	none	0.85	1370–1930	0.8–3.0	+	–	–	–	[170]

Note. For liquid fuels, the nitrogen content in the fuel is indicated in weight percentages, while for gaseous fuels it is indicated in volume percentages.

A significant decrease in the yield of NO_x is achieved as a result of the interaction of the nitrogen oxides formed with soot:

$$2NO+C\rightarrow N_2+CO_2.$$

A decrease in the NO_x concentration in the effluent gases on apparatus of this type can occur also by virtue of the interaction of NO with CO [172].

The nature of the catalyst exerts a major influence on the yield of fuel nitrogen oxides. The use of oxide catalysts makes it possible to attain lower degrees of conversion of bound nitrogen into NO_x than in the case where catalysts based on noble metals are employed. In the single-stage combustion of a gaseous fuel with added NH_3 in an excess of air [177], the degree of conversion of bound nitrogen into NO_x reaches 70–80% in the presence of the NiO/ZrO_2 catalyst and 90–95% in the presence of the Pt/Al_2O_3 catalyst (combustion temperature 700–900 K). In the multistage combustion using the NiO/ZrO_2 catalyst in the first stage, the degree of conversion of bound nitrogen into NO_x is 10%, while in the presence of the platinum catalyst 35% of the fuel nitrogen is converted into oxides.

The combustion of mixtures of propane with ammonia has been studied on a catalyst containing chromium and cobalt oxides [178]. The temperature profile in the catalyst bed affects the yield of nitrogen oxides. Under optimum conditions with $\alpha > 1$, it is possible to decrease the degree of conversion of bound nitrogen into NO_x to 5–20%.

With increase in pressure, the yield of NO_x can both increase [179] and decrease [172,176]. Data concerning the influence of the nitrogen content in the fuel on the degree of conversion of bound nitrogen into oxides are just as uncertain: an increase in the concentration of bound nitrogen (in the form of NH_3) in the gaseous fuel was accompanied by a decrease [171] and an increase [175] in X_{NO_x}. An increase in the pyridine content in the liquid fuel resulted in some decrease in X_{NO_x} [179]. Overall, the problem of reducing the fuel NO_x waste in the combustion of fuels in a stationary catalyst bed requires further work.

The characteristics of the formation of nitrogen oxide in the combustion of nitrogen-containing fuels in a fluidised bed of granulated catalysts, specially developed for catalytic heat generators, have been examined [164,183–187]. The experiments were performed on a pilot apparatus with a power of 20 kW. Experiments were performed initially on the combustion, in catalytic heat generators, of fuels virtually free of bound nitrogen in order to determine the possible contribution of thermal NO_x to the overall amount of nitrogen oxides. In the combustion of n-decane and diesel and furnace fuels on catalysts containing 5 and 30% $CuCr_2O_4$

on γ-Al_2O_3, the observed values of c_{NO_x} did not exceed 10 p.p.m., i.e. the equilibrium concentration calculated for 1000 K and $\alpha = 11$ [164].

The characteristic features of the formation of fuel NO_x were investigated by combusting both a fuel with the natural abundance of bound nitrogen of 0.1% (masouts M100 and M40) and specially prepared mixtures of fuels with nitrogen-containing additives. In the combustion of diesel fuel with added pyridine, giving rise to a nitrogen concentration up to $N_f = 1$ wt.%, the CO_2 and NO_x concentration profiles increased in parallel along the reactor height and attained a constant level at the height corresponding to the complete conversion of the fuel (500–600 mm) [164]. Nitrogen oxides were formed in the catalytic oxidation of the fuel in the fluidised catalyst bed and additional formation of NO_x over the bed was not observed.

In the combustion of model mixtures of isopropyl alcohol with nitrogen-containing compounds (caprolactam, acetonitrile, monoethanolamine, or pyridine) the degree of conversion of bound nitrogen into NO_x was determined mainly by the combustion conditions and depended little on the nature of the oxidised nitrogen-containing substance. At a catalyst bed temperature of 1023 K, $N_f = 1$ wt.%, and $\alpha = 1.22$, the degree of conversion of nitrogen into NO_x is 11–15% [185,187].

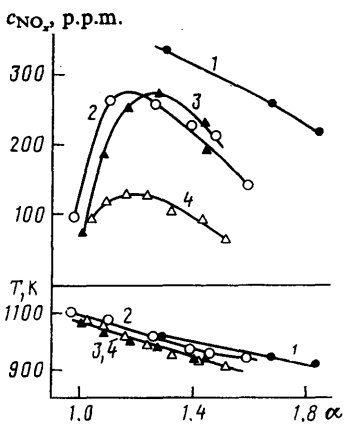


Figure 4. Dependence of the NO_x concentration and catalyst bed temperature on α in the combustion of a mixture of diesel fuel with pyridine [187] in the presence of different catalysts: *1*, Pt/γ-Al_2O_3; *2*, chromium oxide catalyst; *3*, 25% $CuCr_2O_4/\gamma$-Al_2O_3; *4*, 5% $CuCr_2O_4/\gamma$-Al_2O_3.

The dependence of the NO_x concentration on α was investigated in the combustion of masouts M40 and M100 with added ammonium nitrate and pyridine in the presence of the $CuCr_2O_4/\gamma$-Al_2O_3 catalyst [183,184]. The curves obtained had a maximum and the concentration of NO_x fell as α approached unity. For a bound nitrogen content of 0.2%, the NO_x concentration was 40–80 p.p.m., while for $N_f = 1$% it amounted to 80–150 p.p.m., which is much lower than in the flame combustion of such fuels [4,21]. The degree of conversion of bound nitrogen into NO_x is between 5 and 15%.

The dependence of X_{NO_x} on N_f was investigated by combusting mixtures of isopropyl alcohol with pyridine and of diesel fuel with pyridine [185,187]. With increase in N_f, the NO_x concentration rises, but the degree of conversion X_{NO_x} falls. Industrial waste with a high content of bound nitrogen can be made safe by its combustion in a catalytic heat generator. Even for $N_f = 8$%, the NO_x concentration is less than 520–540 p.p.m., which is significantly lower than the value 3000–5000 p.p.m. expected in the flame combustion of a similar mixture [185,187].

The nature of the active component of the catalyst used in the catalytic heat generator also affects the formation of NO_x in the combustion of nitrogen-containing fuels (Fig. 4). Aluminoplatinum catalysts afford the greatest amount of nitrogen oxides, while oxide catalysts produce a smaller amount of such oxides. In full agreement with experiment [186,187], a decrease in the concentration of the active component of the deposited catalyst promotes a decrease in the emission of nitrogen oxides (Fig. 4). An increase in temperature leads to an increase in the concentration of nitrogen oxides (as the temperature rises by 150 K, the NO_x concentration is doubled) [187].

We shall now analyse the problem of the amount of nitrogen oxides evolved in the combustion of fuels in a catalytic heat generator and in the traditional flame combustion [1,2,21] relative to the c_{NO_x} level calculated from the equilibrium constants of the reaction $N_2 + O_2 \rightleftarrows 2NO$ for $\alpha = 1.1$ (Fig. 5). In the temperature range (1500–2000 K) where real combustion takes place, the calculated equilibrium NO_x concentration varies from 400 to 2500 p.p.m.[1] The NO_x concentrations observed in flame combustion are lower than these values, because, owing to the insufficiently long residence time of the fuel–air mixture in the combustion chamber, equilibrium cannot be attained. In the catalytic combustion, the yield of thermal NO_x is extremely low (less than 5 p.p.m.) while the concentration of fuel NO_x is higher than the equilibrium values corresponding to the temperature range of this method of combustion but is lower by a factor of 5–10 than in flame combustion in devices with a combustion chamber.

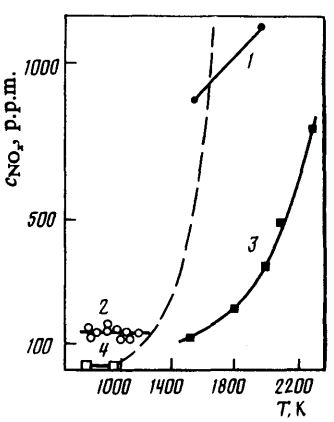


Figure 5. Dependence of the concentrations of fuel (curves *1* and *2*) and thermal (curves *3* and *4*) NO_x on temperature in the flame (curves *1* and *3*) and catalytic (curves *2* and *4*) combustion ($\alpha = 1.1$); the data for the fuel NO_x were obtained at $N_f = 1$ wt.%; dashed line—equilibrium NO_x concentrations [1,2,187].

Catalytic combustion can be used successfully in various domestic and industrial combustion chamber devices in order to decrease the degree of incomplete chemical combustion and the amount of thermal NO_x waste. However, the problem of reducing the fuel NO_x waste formed in the combustion of fuels containing bound nitrogen in devices with platinum catalysts operating at high temperatures and under severe thermal conditions has not yet been solved. The study of the kinetics of the oxidation of nitrogen-containing compounds on solid catalysts has shown that a decrease in the yield of fuel NO_x can be attained by using oxide catalysts instead of platinum catalysts, by reducing the temperature, and by adjusting the coefficient of the excess of air to values close to unity. A decrease in temperature is usually accompanied by a fall in the power and efficiency of the device. The use of a fluidised bed in catalytic heat generators makes it possible to carry out technological processes with much heat evolution and at a low temperature in the combustion zone (770–1070 K) by combining the heat evolution and heat removal processes in a single catalyst bed. It is important to emphasise that a decrease in the concentration of nitrogen oxides in catalytic combustion is ensured by the method of combustion itself and by the selection of the optimum process conditions and catalysts. There is then no need for the expensive removal of nitrogen oxides from smoke gases.

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Procedures for making gaseous industrial waste safe

Yu Sh Matros, A S Noskov

ABSTRACT. The application of various methods (adsorption, absorption, thermal afterburning, catalytic purification, and others) for the removal of sulphur and nitrogen oxides, toxic organic compounds, hydrogen sulphide, and carbon monoxide from industrial waste gases is described. Much attention is devoted to the catalytic procedure for making the gases safe using an energy collecting non-stationary method (reversible process).

The advantages and limitations of various gas purification methods are considered.

The bibliography includes 279 references.

Contents

I. Introduction 989
II. Absorption methods 989
III. Adsorption methods 990
IV. Condensation methods 992
V. Membrane methods 992
VI. Thermal afterburning 992
VII. Catalytic methods 994
VIII. Non-catalytic chemical methods 999
IX. Biochemical methods 1000
X. Conclusion 1000

I. Introduction

The formation of gaseous compounds contaminating the atmosphere is caused mainly by the combustion of mineral fuels, industrial technological processes, and natural phenomena. The development of industry has led to a constant increase in the amount of waste. Thus in the USA the dominant contribution to the sulphur dioxide waste (76%) is made by fuel combustion processes in stationary plants. Carbon monoxide enters the atmosphere to a large extent as a result of the operation of the engines of automobiles and other means of transportation (76%). Industrial organic solvents and petroleum gas processing are sources responsible for 29% of the emitted hydrocarbons, while 38% is contributed by transport. In the Federal Republic of Germany, the fraction of transport waste in 1982 was 55%, while that of waste generated by thermal electric power stations (TES) was 28% relative to the total amount of nitrogen oxides of industrial origin. In terms of the SO_2 (~150 million tonnes annually) and hydrocarbons (~70 million tonnes annually) ejected into the atmosphere, industry has already become comparable to natural sources.[1,2] The main contribution to the contamination of the atmosphere by carbon monoxide (300 million tonnes annually) also comes from man's industrial activity.[1] Only the amount of nitrogen oxides originating from natural sources is approximately ten times greater than that arising from anthropogenic sources (700 million tonnes annually against 50 million tonnes annually).[1,2] However, as a result of the localisation of this type of waste at sites with the highest population density their negative effect is considerable.

The main procedure for reducing the amount of toxic waste ejected into the atmosphere in technological processes involves the improvement of the latter. For example, in order to reduce the sulphur dioxide waste in the combustion of fuel, use is made of the preliminary elimination of sulphur and its binding during the combustion process.[1,3–6] A decrease in the formation of nitrogen oxides is achieved using a stepwise combustion of fuel,[7,8] with the aid of special types of burners,[8–10] and by a number of other measures. However, in most cases the improvement of technological methods, especially the existing methods, does not permit the attainment of the permissible norms and special additional purification of waste gases to remove toxic impurities is necessary.

The industrial methods for making safe gaseous waste can be divided into the following main groups:[1,11] (1) condensation; (2) absorption; (3) adsorption; (4) thermal combustion; (5) chemical conversion of impurities into non-toxic or readily utilisable compounds; (6) catalytic methods; (7) membrane separation; (8) biochemical purification.

II. Absorption methods

Absorption involves the dissolution of the gaseous component in a liquid solvent. In practice absorption is usually accompanied by a rapid chemical reaction in the liquid phase.

Absorption systems can be divided into aqueous and non-aqueous. In the latter case, involatile organic liquids are usually employed. A liquid is used for absorption only once or it is regenerated with the isolation of the contaminant in a pure form.[1,11] Schemes with a single employment of the absorbers are used in those cases where absorption leads directly to the formation of the finished product or intermediate. As examples, one may point to the synthesis of inorganic acids (absorption of SO_3 in the manufacture of sulphuric acid,[12] the absorption of nitrogen oxides with formation of nitric acid[13]), salts (absorption of nitrogen oxides by alkaline solutions with formation of nitrite-nitrate liquors, absorption by aqueous lime or limestone solutions with formation of calcium sulphate[14]), and other substances (absorption of NH_3 by water to obtain aqueous ammonia[15]).

Schemes with the repeated use of absorbers (cyclic processes) are more common. They are used to trap hydrocarbons,[11] to eliminate SO_2 from TES smoke gases,[16] to eliminate hydrogen sulphide from venting gases by the iron-soda method with formation of elemental sulphur,[17] and for the monoethanolamine removal of CO_2 from gases in the nitrogen industry.[15]

Depending on the method used to generate the phase contact surface, one can distinguish surface, bubbling, and spraying (atomising) types of absorption apparatus. In the first group of

devices, the contact surface between the phases consists of a liquid mirror or of the surface of a flowing film of liquid. Packed absorbers, in which the liquid flows down the surface of the packing immersed in it and made up from bodies of different shapes are also included in this group. In the second group of absorbers the contact surface is increased by dispersing the gas streams in the liquid into bubbles and jets. Bubbling is achieved by passing the gas through a liquid-filled apparatus or in apparatus of column type with plates of different kinds. In the third group, the contact surface is created by spraying the liquid into the bulk of the gas. The contact surface and the efficiency of the process are determined overall by the degree of dispersion of the sprayed liquid.

Packed (surface) and bubbling plate absorbers have come to be most widely used.[1,16] The trapped component must be readily dissolved in the absorption medium and frequently interacts chemically with water, as happens, for example, in the elimination of HCl, HF, NH_3, and NO_2 from gases. In order to absorb gases with a lower solubility (SO_2, Cl_2, H_2S), use is made of alkaline solutions based on NaOH or $Ca(OH)_2$. The addition of chemical reagents increases in many instances the efficiency of the absorption by virtue of the occurrence of chemical reactions in a film.[1,18] An increase in the degree of purification can also be achieved by carrying out the absorption process in two stages.[19] There exist various modifying additives to aqueous solutions. Thus coal tar is introduced to trap naphthalene or formaldehyde,[20,21] phenol is trapped by sodium hydroxide solutions,[22] and the use of alkali metals and tertiary C_3-C_{20} amines is effective for the elimination of phosgene from gases.[23] Gases containing HCl, NH_3, and hydrocarbons are purified by being absorbed in aqueous solutions of formaldehyde and subsequent oxidation.[24] The application of solutions of urea or its derivatives is recommended for the trapping of formaldehyde.[25] Systems in which finely dispersed activated charcoal is added to the absorption liquid to increase the trapping efficiency should be mentioned specially.[26–28] In order to improve the removal of organic substances from gases, an oxidant is also introduced simultaneously into the system.

Absorption or more precisely absorption-chemical procedures for making safe the smoke gases from TES, metallurgical industries, and other objects by removing SO_2 has come to be widely used recently. The first large industrial apparatus in the world for the removal of sulphur, operating on the basis of the wet limestone method and having a productivity corresponding to 3 million $m^3\ h^{-1}$ of combined gases, began to operate at the Magnitogorsk Metallurgical Unit in 1961. At the present time, this plant traps about 100 000 tonnes of sulphur dioxide annually.[14] The volume of TES gases freed from SO_2 now reaches $10^9\ m^3\ h^{-1}$ in Japan, the USA, and the Federal Republic of Germany and the total number of plants is approximately 250.[14,29]

Absorption methods in which a calcium sorbent is employed are most widely used in the purification of TES smoke gases.[30–32] When the wet lime (limestone) process is used,[1,23] a sludge consisting of calcium sulphites and sulphates, which can be stabilised (for example, by heating) in the form of gypsum, is produced. Smoke gases freed from ash pass to a plate absorber irrigated with water containing finely ground limestone and neutralisation products. The purified gases pass through a spray trapping unit and after heating (to prevent condensation) are ejected into the smoke tube. After the absorption of SO_2, the acidified liquid passes through a compartment to which a fresh limestone suspension is added. After the accumulation of 10–15 wt.% of calcium salts in the irrigating liquid, part of the suspension is removed to special compartments and subsequently the resulting sludge is eliminated from the system. In order to produce gypsum, the scheme is supplemented by a line involving the oxidation of calcium sulphite to calcium sulphate and the removal of the salts. Under industrial operating conditions, a stable removal of SO_2 from gases with 90% efficiency is achieved.

A semi-dry method (spray absorption) for the removal of SO_2 from smoke gases[1,14,31] is used in the combustion of types of coal containing between 0.5 and 1.5 wt.% of sulphur. The principal stage is the absorption of SO_2 by droplets of a lime solution evaporating in the waste gases. For this purpose, smoke gases are passed through a spray absorber, whose geometry and hydrodynamic conditions ensure the complete evaporation of the droplets. The reaction product is a dry mixture of calcium sulphite and sulphate. The principal technical difficulty consists in the organisation of the effective mass exchange between the liquid and the smoke gases. For example, the spray driers of the Lurgi company make it possible to obtain droplets 80–100 μm in size with an overall surface of 60 m^2 per litre of liquid.[34] The absence of waste water and the formation of the product in a dry form make it easier to use this method in industry.[16]

Organic absorbents such as dimethylaniline, amines,[1] the dimethyl ether of tetraethylene glycol, and the dimethyl ether of poly(ethylene glycol)[2] are used in non-aqueous systems. Hydrocarbon oils are employed to remove mercaptans.[35–37] Absorption by organic solvents has proved to be most effective for the elimination of organic gaseous impurities. An obligatory condition is naturally a low pressure of the vapour of the wash liquid itself (not more than 1 Pa).

In the vast majority of cases, the non-aqueous absorber and the absorbed substance do not interact chemically. A typical example of the use of the absorption method may be the removal of benzene vapour from gases by means of a heavy oil (for example, hexadecane).[37] After absorption, the absorbing solution is heated and transferred to the desorber. Since water does not mix with benzene and the oil, the desorption is carried out using hot steam. The vapour emerging from the desorber is directed to a condensing unit to trap the absorber and partly water vapour. After their separation in the separator, the condensed absorber is returned to the cycle. The mixture of water vapour and benzene is recondensed. The non-condensing gases are separated from the liquid in the separator and liquid benzene is separated from water using the difference between their densities.

In conclusion we may note that absorption is most widely used in industry to trap acid components from effluent gases and for the removal of SO_2 from smoke gases.

III. Adsorption methods

Adsorption methods constitute one of the most widely used procedures for the protection of air from contamination. In the USA alone, tens of thousands of adsorption systems have been introduced and used successfully.[38] The principal industrial adsorbents are activated charcoals, complex oxides, and impregnated sorbents. Activated charcoal (AC) is neutral in relation to polar and non-polar molecules of the adsorbed compounds. It is less selective than other adsorbents and is one of the few adsorbents suitable for use in moist gas streams. Activated charcoal is used in particular for the removal of substances with an unpleasant smell from gases, for the recovery of solvents, etc.[1,39]

Oxide adsorbents (OA) exhibit a higher selectivity in relation to polar molecules by virtue of the intrinsic non-uniform distribution of the electrical potential. Their disadvantage is the decrease in efficiency in the presence of moisture. Silica gels, synthetic zeolites, and aluminium oxides belong to the class of oxide adsorbents.

Impregnated adsorbents (IA) are divided into three groups:

(1) Adsorbents impregnated by a chemical reagent. As a result of the occurrence of a chemical reaction on such impregnated adsorbents, the adsorption of substances which are difficult to adsorb is facilitated. For example, the introduction of iodine improves the adsorption of mercury or ethylene vapour on activated charcoal.

(2) Impregnated adsorbents in which the impregnating substance plays the role of the catalyst of the extensive oxidation of the trapped impurities. Catalysis is ensured, for example, by introducing into the activated charcoal oxygen-containing compounds promoting the oxidation of impurities in oxygen-free gases.

(3) Periodically activated impregnated adsorbents. The activation is carried out, for example, by the cyclic increase in temperature after the completion of the adsorption of impurities.

It is possible to differentiate the following principal ways of carrying out adsorption purification processes.[39–41]

1. After adsorption, desorption is carried out and the trapped components are extracted for reuse. Various solvents,[11] carbon disulphide in the manufacture of artificial fibres,[41] and a number of other impurities[42] are trapped in this way.

2. After adsorption, the mixtures are not neutralised but are subjected to thermal or catalytic afterburning.[39,41,43,44] This method is used to purify the gases from chemopharmaceutical and paint and varnish undertakings, the food industry, and a number of other industries. This variety of adsorption purification is economically justified by low concentrations of the contaminating substances and (or) when the contaminants consist of numerous components.[39,41]

3. After purification, the adsorbent is not regenerated but is, for example, stored or combusted together with the strongly chemisorbed contaminant.[1] This procedure is suitable when cheap natural adsorbents are employed.[42]

To desorb the impurities, the adsorbent is heated, evacuated, or flushed by an inert gas while the impurities are displaced by a more readily adsorbed substance, for example water vapour.[1,40,41] Attention has been concentrated recently on the desorption of impurities by evacuation.[45–51] Under these conditions, it is frequently possible to utilise them readily.

A wide variety of different types of apparatus have been developed for adsorption processes.[1,39,41,52,53] The most common are adsorbers with a fluidised bed of a granulated or honeycomb adsorbent. The continuity of the adsorption and adsorbent regeneration processes is ensured by using apparatus with a fluidised bed. The theory of adsorption in fluidised beds has been examined in greatest detail by Krishnaiah and co-workers.[54,55] There also exist adsorbers with a "flowing" adsorbent. By arranging appropriately the sites where the particles are introduced and removed, it is possible to organise the "flow" of the adsorbent along different lines. Adsorbents with a rotating bed are more rarely used in practice.[40,56,57] A variety of the process in which the adsorbent is sprayed into the stream of the gas being purified to produce a finely dispersed aerosol with subsequent trapping and regeneration of the latter has been proposed.[58] Fibrous sorption-active materials have been used increasingly in recent years.[57,59–66] Differing little from granulated adsorbents in their capacity, they are greatly superior to the latter in terms of a number of other parameters. For example, they are distinguished by high thermal and chemical stabilities, the uniformity of their polar structure, the large volume of micropores, and a higher mass transfer coefficient (greater by a factor of 10–100 than for granular sorption materials).[52] Devices employing fibrous materials occupy a much smaller area.[59,60] The mass of the adsorbent in procedures employing fibrous materials is smaller by a factor of 15–100 than in the case where an activated charcoal is used while the mass of the apparatus is smaller by a factor of 10. The resistance of the bed does not then exceed 100 Pa. The technical-economical parameters, of the existing processes can be increased also by the optimum organisation of the desorption stage,[67,68] For example, by means of a programmed temperature rise.[68]

The high efficiency of purification on activated charcoals with a honeycomb (cellular) structure, which exhibits improved hydraulic characteristics, is noteworthy. Such sorbents can be obtained by depositing specific compositions with a charcoal powder on a synthetic resin foam[45,69–71] or by foaming a mixture of specified composition containing the activated charcoal.[69] They can also be produced by burning away a filler from a mixture incorporating an activated charcoal together with a binder.[71]

Yet another way of improving adsorption purification methods involved the development of new modifications of adsorbents—silica gels and zeolites with improved thermal and mechanical stabilities. However, the hydrophilic nature of these adsorbents makes their application difficult. In order to make silica gel hydrophobic, it is modified, for example, by high-molecular-weight organic compounds.[72,73] High-silica and ultrahigh-silica zeolites (UHS-zeolites) in which the $SiO_2:Al_2O_3$ ratio can reach 100 and above making them more hydrophobic, were synthesised in recent years.[52]

The largest-scale adsorption purification apparatus is apparently used in the manufacture of artificial fibres.[38] A chemical fibre plant with average productivity ejects approximately 1.5 million $m^3 h^{-1}$ of venting gases containing H_2S and CS_2. Depending on the H_2S concentration two modifications of the adsorption method for the purification of these gases are distinguished. Since in the presence of oxygen hydrogen sulphide may be oxidised on activated charcoal to sulphur and sulphuric acid, at high H_2S concentrations the gases are subjected to preliminary absorption purification to a residual content of 20–50 mg m^{-3}. After this CS_2 is eliminated by the adsorption method. At low initial H_2S concentrations (not more than 3 g m^{-3}), there is a possibility of the joint removal of hydrogen and carbon sulphides by the adsorption purification of gases. The sulphuric acid formed on the surface of the adsorbent-catalyst is periodically neutralised, for example, with ammonia, after which the salts are washed away with water and the sulphur is removed by washing with solvent (usually with carbon disulphide).

The adsorption purification methods have found an application also in the detoxification of industrial gases by removing mercury vapour.[74] In this case, impregnated charcoals are used for the purification. Activated charcoal is usually impregnated with hydrogen halides (HCl and HI).

Adsorption methods for the extraction of solvents, including organochlorine solvents, from effluent gases have come to be most widely used.[38,40,41,52,53,75] This is associated with the high efficiency of the gas purification process (95–99%), the absence of chemical reactions leading to the formation of secondary contaminants and the short period in which the recovery apparatus pays for itself (usually 2–3 years) as a result of the reuse of the solvents and the long (up to 10 years) useful life of the activated charcoal.[40] Active

studies are being prosecuted on the adsorption extraction of sulphur and nitrogen oxides from gases,[76–78] but these have not been applied on an industrial scale so far.

IV. Condensation methods

Condensation is used to remove impurities from gases by cooling them to a temperature below the dew points of the substances to be removed. This method is most effective and is most often used for the removal (utilisation) of hydrocarbons and other organic compounds which have fairly high boiling points under the usual conditions and are present in the gas phase in considerable amounts.[2,79] The elimination of such contaminants is achieved in condensers with water and air cooling. For more volatile contaminants, two-stage condensation is used: water cooling in the first stage and cooling to low temperatures in the second.[11] Cooling to low temperatures solely with the aim of removing contaminants is not effective, since the purification process cannot be achieved with a sufficient degree of completion. For example, even at 213 K and atmospheric pressure the residual concentrations of different solvents are as follows (mg m^{-3}): 1775 for acetone, 275 for methanol, 8 for toluene, and 0.75 for isopropyl alcohol.[11] In most cases condensation can be usefully treated as a preliminary stage serving for the isolation of valuable solvents and for the reduction of the amount of contaminants before the subsequent treatment of gases.

Condensation is carried out both with direct contact and via indirect cooling. In the former case, the gas to be purified is brought into direct contact with the cooled liquid, while in the latter a tubular surface condenser is used. In direct cooling, the subsequent separation of the heat exchanger and of the trapped impurities is important. For this purpose, one selects components such that under certain conditions they form as a result of phase transitions constituents which can be readily separated.[80,81] Condensation is also carried out by the adiabatic expansion of gases supplied under pressure for purification.[82] In order to separate different impurities present in the cooled gases, ionisation and fractionation in an electric field are employed.[83]

The application of the condensation method is complicated by the formation of a mist on extensive cooling of the gas to be purified. This occurs when the rate of heat transfer greatly exceeds the rate of mass transfer and the main bulk of the gas is cooled to a temperature appreciably below the dew points of the condensed impurities. To prevent mist formation, indirect condensation is used, since in this case the main bulk of the gas is in contact with cooled surfaces (liquid drops or film) and condensate particles are not formed in the bulk phase.[11]

V. Membrane methods

Membrane separation processes include stages involving the transfer of the initial mixture to a membrane, the permeation of the mixture components into the membrane, their transfer through the membrane, and the subsequent removal of the separated products.[84] In practice one uses metallic membranes based on palladium, its alloys, silver, and ruthenium as well as synthetic membranes[85] and ceramic-based membranes.[86] Synthetic membranes are made from polymers based on styrene, acrylonitrile, isoprene, silicone, and other elementary components.[85]

Membrane methods have already proved very useful in the manufacture of pure hydrogen,[86] in the extraction of helium from natural gas,[87] and in the purification of gas waste from atomic power stations.[88]

The solubilities of the following substances and their permeation into polymers have been investigated recently: toluene in polystyrene,[89] alcohols, dichloromethane, and benzene in polyvinylpyridine,[90] ethyl acetate, acetone, methyl chloride, and ethanol in cellulose nitrate,[91] and toluene, xylene, and cyclohexane in 1,2-polybutadiene.[92] It has been shown[93] that the rates of permeation of the vapours of various organic substances through polypropylene and Teflon films are tens and hundreds of times greater than the rate of permeation of water (toluene/water = 200 at 60 °C; n-heptane/water = 360). This makes it possible to create gas purification membrane systems. For example, in order to extract organic solvents from air discarded from painting chambers,[11,94] the air stream is passed through a membrane module whose material consists of polydimethylsiloxane on a polysulphone support. The vapours of organic solvents diffuse across the membrane, while the air "depleted" in the solvent circulates through the painting chamber. A vacuum pump creating a rarefraction to the extent of 10^{-3} Pa ensures effective transport through the membrane. The solvent vapour is then condensed in the heat exchanger. The air flow rate is ~ 500 m^3 h^{-1} and the content of the solvent in the air stream is ~ 20 g m^{-3} at the inlet, the amount of extracted solvent is ~ 10 kg h^{-1}, the surface area of the membrane is ~ 80 m^2, and its useful lifetime is 2 g. The necessary power of the pump required to generate the required vacuum is 10 kW.

Composite membranes, whose permeability to solvents is 60–160 times greater than their permeability to nitrogen, have been developed.[95] This makes it possible to ensure a high efficiency of membrane and various combined procedures for the purification of gases. For example, membrane separation and absorption trapping have been used in succession.[96]

VI. Thermal afterburning

Afterburning constitutes a method for making gases safe by the thermal oxidation of various harmful substances, mainly organic, to virtually harmless or less harmful materials—mainly CO_2 and H_2O. The usual afterburning temperatures for the majority of compounds are in the range 750–1200 °C. The application of the thermal afterburning method makes it possible to attain 99% purification of gases.[11,97] The small size of the devices, the simplicity of their operation, and the low operating costs even at high concentrations of the impurities have led to the extensive application of this method. For example, more than 2000 thermal afterburning devices operated in the USA in the 1970's.[2]

When the possibility and usefulness of thermal detoxification methods are considered, it is essential to take into account the nature of the combustion products formed. The products of the combustion of gases containing sulphur, halogen, and phosphorus compounds can be more toxic than the initial gaseous waste. In this case, additional purification is essential. Thermal afterburning is extremely effective in making safe gases containing toxic substances in the form of solid inclusions of organic origin (soot, carbon particles, sawdust, etc.).[2,98]

The most important factors determining the usefulness of thermal detoxification are the expenditure of energy (fuel) to ensure high temperatures in the reaction zone, the calorie content of the mixture

subjected to detoxification, and the possibility of preliminary heating of the gases being purified. An increase in the concentration of the mixtures subjected to afterburning leads to an appreciable diminution of the consumption of fuel. In some cases the process can take place under autothermal conditions, i.e. the working conditions are maintained solely by the heat of the extensive oxidation reactions of the harmful impurities and by the preliminary heating of the initial mixture by the detoxified effluent gases.

There exist several different systems for thermal detoxification differing from one another by the process temperature, the hydrodynamic conditions in the reaction zone, and the residence time of the gases in the reaction zone.[2,11,99–101] Chamber furnaces, furnaces with cyclone movement of gases, regenerative devices for thermal detoxification, apparatus with flow mixing, and detoxification systems in technological apparatus (for example in boilers) can be distinguished.

Box furnaces[2,98] are some of the first industrial thermal purification devices. The working space within the furnace is usually divided into two chambers: the chamber for the combustion of the fuel introduced into the system and the mixing chamber where the air to be purified is introduced. The hydrodynamic conditions in the above zones within the furnaces differ significantly and special mixing of the streams is therefore required. The residence time of the gases in the mixing chamber is 3–5 s and the specific consumption of heat on the detoxification process is 270–280 kcal per m^3 of the gas to be purified. Thermal detoxification furnaces using the cyclone gas flow principle are nowadays more common. The cyclone principle ensures vigorous mixing of the streams and hence effective afterburning for shorter residence times of the gases in the reaction chamber (0.1–0.5 s) than in box furnaces. Such furnaces are used for the afterburning of gases in the manufacture of bitumen, synthetic aliphatic acids, in petroleum processing factories, and in current lead enamelling workshops of electrotechnical undertakings. The cyclone gas flow permits an appreciable reduction of the consumption of heat (to 200 kcal per m^3 of the purified gas) compared with the afterburning in a box furnace.[2,98,102,103]

Devices with flow mixing of the components to be detoxified are differentiated as a separate group of apparatus. The principal element of the design of such apparatus is a burner with a stabiliser made in the form of a poorly streamlined body which gives rise to a high turbulence.[2] The use of such burners, placed within the stream of the gas to be purified, makes it possible to reduce the temperature of the extensive purification of gases ranging from CO to CH_4 compared with box furnaces by 150–200 °C.

In many instances, oxygen-containing waste is combusted in combustion chambers of boiler and other technological aggregates[98,104,105] where the contaminated air is used to generate the blast. The degree of elimination of organic acids and aldehydes from gases by this procedure reaches 99–100%.[98] Thermal detoxification processes are used in the manufacture of technical carbon for the afterburning of waste gases whose composition is usually (vol.%) 7–8 H_2, 6–7 CO, 0.5–0.7 CH_4, 2–3 O_2, 2 CO_2, 40 N_2, and 40 H_2O. Furthermore, these gases contain up to 2 g m^{-3} of residual soot (carbon). The high heat generating capacity of the gases (360–500 kcal m^{-3}) permits their use as fuel in special boiler aggregates.[106]

One of the most economical and promising methods is believed to be thermal detoxification using heat exchangers capable of being regenerated.[2,107–121] These devices consist of a combustion chamber and two (or more) layers of the regenerative packing. The periodic alteration of the direction of motion of the detoxified gases through the layers of packing or the rotation of the latter for a constant direction of motion of the gases ensure the regeneration of the heat of the hot purified gases and the heating of the initial gas to be purified.[2,110,111,122] The Retherm afterburning devices[108] with a productivity up to 100 000 m^3 h^{-1}, which make it possible to utilise up to 95% of the heat of the gases being purified,[122] have come to be most widely used. Their design rules out the possibility of the release of gas during the switching of the gas streams, which is achieved by employing five regenerative heat exchangers. A similar design has been proposed also in the USSR.[115] When much heat is evolved, it is also possible to utilise the heat given up as a result of the combustion of impurities.[121]

Overall, recent years have been characterised by a vigorous development of thermal detoxification methods based on the regenerative principle of heat exchange.[109–120] In some cases, attempts have been made to combine catalytic and thermal methods by incorporating in the apparatus both burners and layers of extensive oxidation catalyst.[112,118–123] Thermal afterburning has found applications in the most varied branches of industry. Simple versions of afterburning (for example, flame afterburning) are used in metallurgical[98] and chemical (petrochemical) undertakings.[124] Thus thermal afterburning is widely employed for the detoxification of waste gases from cast iron cupolas. The principal combustible component of cupola gases is carbon monoxide, whose content reaches 8–15 vol.%. For CO contents from 11 to 15 vol.% the gas at a temperature of 300–350 °C can be burnt virtually without the consumption of fuel. When the CO content is reduced, an additional supply of natural gas is needed.[98] The converters available at present operate predominantly with the afterburning of the blast gases in the so called cooling units for smoke gases or directly in the flame. The concentration of carbon monoxide in gases changes during the blasting of the converter from 40 to 98%. The temperature of the waste gases is 1100–1400 °C and the residual maximum CO content after afterburning does not exceed 0.2–0.5 vol.%.

Thermal detoxification is used also for the afterburning of the effluent gases from aluminium and electrode industries. The waste generated in this case in the combustion of petroleum coke contains between 12 and 23 vol.% of gaseous combustible components (CO + H_2 + CH_4) and about 20 g m^{-3} of coke dust.[98]

The principal difficulty in using thermal afterburning arises from the formation of secondary contaminants such as nitrogen oxides, chlorine, SO_2, etc. In order to reduce the NO_x concentration, two-stage combustion is employed; in the first stage, where the process is carried out in the presence of a deficiency of oxygen, a large residual CO content is retained, while in the second stage all the combustible impurities are subjected to extensive oxidation.[125–127] A decrease in the emission of nitrogen oxides is also promoted by recirculation of gases and by the decrease in their preliminary heating.[97,99]

Thermal afterburning of gases containing organochlorine compounds is especially important for chemical industries.[128–137] In the presence of a deficiency of oxygen,[132,134,135,137] organochlorine compounds are oxidised not to elemental chlorine but to HCl, which can be readily bound by alkali. Thermal decomposition in plasmatrons[132] or in inducton arc furnaces[137] is also used for the afterburning of chlorinated hydrocarbons. In order to reduce the process temperature and the amount of chlorine formed, ultraviolet irradiation is employed[133] as well as turbulent afterburning.[136]

Sometimes the gases are passed over the surface of fused iron[138] or aluminium[139] to achieve the afterburning of toxic impurities. One cannot rule out the possibility that the oxide film formed on the metal surface plays the role of the catalyst in such cases.

Much attention has been devoted to the intensification of the existing thermal afterburning processes, for example via the thermal oxidation of impurities in a fluidised bed of heat resistant particles[140,141] or by employing electric arc furnaces.[142] The thermal gas afterburning process, under the conditions of a variable rate of their supply and a variable concentration of the impurities, can be stabilised by employing in the high-temperature zone of the furnace a packing comprising an inert (for example, ceramic) material.[143] Such packing ensures simultaneously a better mixing of the streams and increases the degree of afterburning.

The possibility of using thermal afterburning for making safe non-standard methane–air mixtures ejected from coal mines has been discussed recently. During the ventilation of the amines approximately seven hundred million m^3 of mixtures containing less than 30 vol.% of methane (conditioned mixtures) and about four thousand million m^3 of air containing between 0.5 and 0.75 vol. of methane (non-conditioned mixtures[98]) are ejected into the air annually. The combustion of the non-conditioned ejected mixtures together with solid fuel, their enrichment in natural gas, the combustion of weak mixtures using preliminary additional heating, and the connection of sources of coal mine methane to the overall (collecting) network are apparently the most promising procedures.[144]

Thermal methods have found the main application in the elimination of organic impurities from highly concentrated gases, including gases containing mechanical impurities.

VII. Catalytic methods

Catalytic gas purification methods are distinguished by their universality. With their aid, it is possible to free gases from sulphur and nitrogen oxides, hydrogen sulphide, various organic compounds, carbon monoxide, and other toxic impurities. Catalytic methods make it possible to convert harmful impurities into safe ones, less harmful ones, and even useful impurities. They make it possible to process multicomponent gases with low initial concentrations of harmful impurities, achieving high degrees of purification, to carry out the process continuously, and to avoid in most cases the formation of secondary contaminants. The application of catalytic methods is usually restricted by the difficulty of finding and preparing sufficiently cheap catalysts suitable for prolonged use. The heterogeneous-catalytic conversion of gaseous impurities is achieved in a reactor charged with a solid catalyst in the form of porous grains, rings, pellets, or blocks with a nearly honeycomb structure. Chemical conversion takes place on the extensive inner surfaces of the catalysts, reaching 10^3 $m^2 g^{-1}$.

A wide variety of substances can serve as effective catalysts used in practice. They range from minerals, which are used virtually without any preliminary treatment, and simple massive metals to complex compounds with a specified composition and structure. Catalytic activity is usually shown by solids with ionic or metallic bonds and having strong interatomic fields. One of the principal requirements which must be met by the catalyst is the stability of its structure under the reaction conditions. For example, metals should not be converted during the reaction into inactive compounds.[145,146]

Modern detoxification catalysts are characterised by a high activity and selectivity, mechanical strength, and resistance to the action of poisons and temperature. Industrial catalysts, made in the form of rings and blocks with a honeycomb structure, offer a low hydrodynamic resistance and have a high external specific surface.[146]

Catalytic methods for the detoxification of effluent gases in a stationary catalyst bed have come to be most widely used. It is possible to differentiate two fundamentally different procedures for carrying out the gas purification process—under stationary and artificially created non-stationary conditions.

1. The stationary method

Rates of chemical reactions suitable for practical use are attained in the presence of the majority of cheap industrial catalysts at 200–600 °C. After the preliminary removal of dust (up to 20 mg m^{-3}) and various catalytic poisons (As, Cl_2, etc.), the temperature of the gases is usually appreciably lower.

The gases can be heated to the required temperatures by introducing combustible smoke gases or with the aid of an electric heater. After passage through the catalyst bed, the purified gases are released into the atmosphere, which requires an appreciable energy consumption. A reduction of energy consumption can be achieved if the heat of the effluent gases is used to heat the gases entering the purification process. Regenerative tubular heat exchangers are usually employed for heating.

Under certain conditions, where the concentration of combustible impurities in the effluent gases exceeds 4–5 g m^{-3}, the process in accordance with a scheme employing a heat exchanger makes it possible to avoid additional consumption of heat. When reversible exothermic reactions take place, the attainment of a high degree of purification requires the intermediate removal of heat, which appreciably complicates the technological scheme. The processing of gases by the above method is difficult if the gas is supplied at a variable rate and when the concentration of impurities in it is not constant. The presence of an external heat exchange increases the parametric sensitivity of the system and enhances the risk of overheating and sintering of the catalyst even after a slight increase in the concentration of impurities and (or) decrease in the gas flow rate. Such devices can operate effectively only at constant concentrations (flow rates) or when ideal systems for the automatic regulation of the process are employed. These difficulties can be overcome by carrying out the gas purification under non-stationary conditions.

2. The non-stationary method (flow reversal process)

If the stationary catalyst bed is initially heated to a temperature ensuring the occurrence of the chemical reaction at an appreciable rate and the reaction mixture, whose temperature is insufficient for the occurrence of the reaction is directed to it, then after a certain time interval a thermal front is established in the bed.[148,149] It moves at a rate smaller by a factor of 100–1000 than the rate of filtration of the gas through the catalyst. A second feature of the thermal front, consisting in the fact that the difference between the maximum and inlet temperatures can greatly exceed the temperature drop due to the adiabatic heating with complete conversion of the initial mixture (ΔT_{ad}), gives rise to the possibility of a technological application of this phenomenon.

The non-stationary method is illustrated schematically in Fig. 1. It provides for the periodic alteration of the directions of filtration of the gas mixture in the catalyst bed with the aid of valves *1* and *2*.[150] The process proceeds as follows. The catalyst bed is heated initially to a temperature at which the catalytic process proceeds at a high rate. After this, the gas to be purified is supplied to the apparatus at a low temperature (T_{inp}) at which the rate of the chemical reaction is negligible. As a result of direct contact with the solid material, the gas is heated and catalytic reactions begin to

occur at an appreciable rate in the catalyst bed. Giving up its heat to the gas, the layer of the solid material (catalyst) is gradually cooled to the temperature equal to that of the gas at the inlet. Since heat is evolved during the reaction, the temperature in the bed can exceed the temperature resulting from the initial heating. A thermal wave is formed in the reactor and moves in the direction of the filtration of the reaction mixture, i.e. in the direction of the outlet from the bed. Periodic reversal of the direction of the supply of the gas makes it possible to retain the thermal wave indefinitely within the limits of the bed.

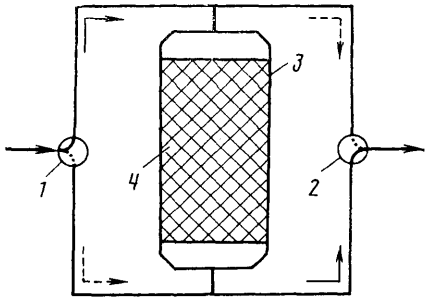


Figure 1. Technological scheme of the gas detoxification process in a non-stationary regime: *1*, and *2*, switching devices; *3*, catalytic apparatus; *4*, catalyst bed.

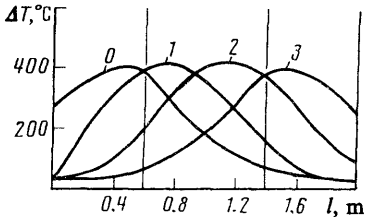


Figure 2. Variation of temperature along the length of the catalyst bed (*l*) during a half-cycle (*O*) before change of direction of filtration; *1*, *2*, and *3*, 6, 15, and 25 min respectively after the change of direction.

Fig. 2 presents typical temperature profiles along the catalyst bed at different times after the change in the direction of the supply of the initial reaction mixture. It is seen that the sections located near the inlet are gradually cooled, while in the middle part of the bed the temperature rises. The increase in temperature is caused by the accumulation of the heat of reaction within the catalyst grains, while the cooling is caused by the removal of heat by the stream of the gas mixture. After 25 min (the half-cycle time), the direction of supply is again altered and subsequently the switching is performed with the same periodicity.

An integral heat balance is maintained in the steady cyclic regime: $T^{av}_{outp} = T_{inp} + \Delta T_{ad} x^{av}_{outp}$ (x^{av}_{outp} is the degree of conversion and T^{av}_{outp} is the average temperature at the outlet). The autothermal nature of the cyclic regime is ensured solely by the heat of the exothermic chemical reaction of the impurities present in the gas undergoing purification.

The principal advantages of the non-stationary method of carrying out heterogeneous catalytic reactions are as follows:[148,150,151]

(1) The autothermal nature of the non-stationary process is achieved with a minimal adiabatic heating of the mixture (of the order of 15 °C).

(2) The complete conversion of the reacting components (or an equilibrium in the case of reversible reactions) is achieved in the catalyst bed.

(3) Variations in the concentrations of the combustible impurities and in the temperature of the input stream and in its volume flow rate do not have a significant effect on the principal parameters of the non-stationary regime in the reactor—the maximum temperature and the degree of conversion—as a consequence of the fairly high heat capacity of the catalytic unit.

(4) Heat exchange takes place within the catalyst bed itself, which not only accelerates the reaction but also ensures the regeneration of heat.

(5) In the processing of gas mixtures, whose adiabatic heating exceeds 100–150 K (which is equivalent to a content of organic substances of 3–5 g m^{-3}), non-stationary devices can become a source of secondary energy resources in the form of steam, hot water, hot gases, etc., obtained as a result of the utilisaton of heat in the zone of maximum temperatures.

(6) In the non-stationary regime, a satisfactory approximation to the theoretical optimum conditions for reversible exothermic reactions is achieved without intermediate heat exchangers. In the case of a fairly close approximation to the theoretical optimum conditions for reversible exothermic processes, the catalytic process can be significantly simplified and a single-stage process can be used instead of a multistage one.

3. The application of catalytic methods in the elimination of toxic compounds from gases

(a) Nitrogen oxides

Among all the possible ways of removing nitrogen oxides from effluent gases, catalytic procedures are most widely used nowadays since they require relatively low capital and operating costs, permit the use of comparatively simple designs, and at the same time are highly effective.[152] Among catalytic methods which have not so far gone beyond laboratory tests, the procedure for the direct decomposition of NO_x into molecular nitrogen and oxygen appears extremely attractive. However, this method is not applicable to oxygen-containing gases. The study of the catalytic activity[40] of metal oxides in the reaction involving the decomposition of NO_x into nitrogen and oxygen showed that in all cases the reaction is retarded by oxygen.[153]

The catalytic methods for the reduction of NO_x adopted in industry can be divided arbitrarily into two main groups: (1) the high-temperature reduction which occurs only in an oxygen-free medium using combustible gases as the reductant; (2) selective catalytic reduction (SCR) whose characteristic feature is the interaction of the reductant employed with nitrogen oxides in the presence of oxygen.

Hydrogen, carbon monoxide, kerosene vapour, and petroleum and natural gases are used for the high-temperature reduction of nitrogen oxides.[154] Nitrogen oxides are reduced to nitrogen, while other reaction products may be water and carbon dioxide. Metals on carriers are employed as catalysts of the high-temperature reduction process. The active components are usually platinum, palladium, and copper–chromium alloys.[155] The process tempera-

ture is normally 300–500 °C.[154] The reduction occurs only in an oxygen-free atmosphere and the first stage is therefore the "burning away" of oxygen. Since the content of nitrogen oxides does not in most cases exceed 0.2 vol.%, the consumption of combustible gases is virtually determined solely by the oxygen content in the smoke gases. In the catalytic "burning away" of 3–8 vol.% of oxygen, the gas temperature increases by 400–1000 K.[154] The disadvantages of the method considered are the high initial reaction temperature, a considerable consumption of the reductant in the removal of oxygen, the cost involved in the utilisation of the heat of the effluent gases, the necessity to maintain a definite temperature process regime, and the possibility of the presence of carbon oxides in the effluent gases as a consequence of the employment of a reducing atmosphere.[152,154,155]

In the selective catalytic reduction of nitrogen oxides, the reductant interacts with NO_x in the presence of oxygen. Under industrial conditions, NH_3 is widely used as the reductant.[156,157] Apart from gaseous ammonia, reagents which evolve it can also be used in SCR processes: various organic nitrogen compounds or the products of the decomposition of the corresponding salts;[158] compounds with amino- or imino-groups;[159] aqueous ammonia solutions.[160]

The activity of the catalyst decreases in the following sequence in reactions involving reduction by ammonia:[154] Pt > MnO_2 > V_2O_5 > CuO > Fe_2O_3 > Cr_2O_3 > CoO_3.

In industry, mainly vanadium-containing catalysts are used for the selective reduction of nitrogen oxides by ammonia.[157] Vanadium pentoxide (V_2O_5), deposited either on Al_2O_3 or TiO_2, possesses a high activity at relatively low temperatures (< 400 °C) and is highly resistant to the action of sulphur oxides, which is very important in the detoxification of sulphur-containing gases from thermoelectric power stations.[161] Attempts are being made to create industrial SCR catalysts based on iron and chromium oxides,[162,163] zeolites,[163–165] and platinum and ruthenium.[162]

The SCR method is applied mainly for the removal of NO_x from gases in the manufacture of nitric acid and in the combustion of fuel. The application of the SCR method to the purification of gases from thermal electric power stations has a number of characteristic features associated with the degree of contamination of the gases by dust, their sulphur content, and their high temperature. Dust-containing gases are purified on catalysts with a ceramic honeycomb structure (blocks) at high linear flow rates—up to 60 m s^{-1}.[166] Catalysts with this structure have walls of identical thickness and form throughout the length of the bed channels with a hydraulic diameter from 2 to 30 mm. The porosity of such a block is 50–80%. Instead of ceramic blocks the active component is sometimes deposited on the surfaces of metallic plates[167] or heat exchange tubes.[168]

In the course of the operation of catalytic reactors for the selective reduction of NO_x, the activity of the catalysts falls both as a result of the blocking of the active surface by dust and the erosion wear of the blocks and as a result of the deposition of salts (sulphites, sulphates, and nitrates). For the partial regeneration of the catalyst, the temperature at the inlet to the bed is periodically raised[169,170] or substances (alcohols, ketones, aldehydes, etc.) promoting the decomposition of the salts are introduced into the reactor.[171] For example, ammonium salts are decomposed by removing the catalyst from the reactor and regenerating it in individual devices.[172–175] Sulphates are eliminated by washing the catalyst with various aqueous solutions.[162]

The principal ways of increasing the cost effectiveness of the SCR processes in thermal electric power stations are a decrease in the energy expenditure and an increase in the useful lifetime of the catalyst. In order to increase the cost effectiveness, rotating heat exchangers are employed nowadays. The hot effluent smoke gases at a temperature of 350–400 °C are mixed with ammonia and are subsequently applied to a rotating plate reactor-heat exchanger. After passage through the reactor-heat exchanger, dust and sulphur dioxide are trapped from the NO_x gases. Fresh air for combustion enters during this period the other half of the apparatus, where it is heated and then supplied to the furnace. The rotation of the heat exchanger is regulated in such a way that a virtually constant temperature is maintained throughout its volume.[1]

Favourable catalyst operating conditions are created naturally when the SCR systems are placed beyond the devices for the removal of dust and sulphur from smoke gases. In this case, one can use much less catalyst and its useful lifetime increases to five years compared with 1–3 years when it operates in dust-contaminated gases.[176] However considerable operating and capital costs involved in heating the gases to 300–350 °C after the removal of sulphur have held back hitherto the extensive industrial application of such procedures. The endeavour to reduce energy expenditure has led in recent years to the use of regenerative heat exchangers in the application of the SCR method.[162,164,165,177]

When the flow reversal process is used to remove nitrogen oxides from gases, the catalyst is placed between inert material beds.[178–180] The ammonia for the reduction of nitrogen oxides is introduced in such a way that the formation of ammonium nitrite and nitrate is virtually ruled out. Certain technological characteristics of the industrial process are presented in Table 1. When the initial content of nitrogen oxides was varied widely and in the presence of a 15% excess of ammonia relative to its required stoichiometric amount, the degree of conversion of nitrogen oxides was not less than 98% with a virtually complete conversion of ammonia. The maximum temperatures in the reactor were in the range 350–450 °C.

The heat evolved in the reduction of NO_x by ammonia in a mixture containing 1 g m^{-3} of nitrogen oxides is sufficient to heat the mixture by 7–10 K. This is sufficient to carry out the process on block catalysts in an autothermal regime. The autothermal nature of the process on granular catalysts is ensured at an initial NO_x concentration of 1.5–2 g m^{-3}.

Table 1. Technical characteristics of industrial equipment for the catalytic detoxification of gases in a non-stationary regime.

Parameter	Oxidation of SO_2 to SO_3 (Ref.183)	Removal of organic compounds	Removal of NO_x by selective reduction
Volume of gases to be purified (10^3 m^3 h^{-1})	35.0	1.0	10–11
Concentration of removable impurities at inlet	2 vol.%	0.5–0.7 g m^{-3} (methanol, phenol, formaldehyde)	4–15 g m^{-3}
Temperature at inlet, °C	30–40	15–20	30–40
Maximum temperature in catalyst bed, °C	480–550	400–550	300–450
Degree of conversion (purification), %	95–97	Methanol—99.9; formaldehyde—99.6; phenol—97.0	98–99
Period between reversals of direction, min	20	30–45	5–25

(b) Sulphur dioxide

Sulphur dioxide, whose concentration is not less than 0.5–0.7 vol.% in effluent smoke gases, is trapped in the vast majority of cases by absorption-chemical methods.[1,14,16] At a SO_2 concentration in excess of 1 vol.%, its utilisation in the form of sulphuric acid or elemental sulphur is economically justified. In order to obtain the acid, sulphur dioxide is oxidised in the presence of a catalyst to SO_3, which is absorbed by a solution of sulphuric acid in a scrubber.[12,181,182] The effluent gases from smelting furnaces for non-ferrous metals, in which the SO_2 concentration is between 4 and 11%, are usually converted into sulphuric acid.[181] Non-ferrous metallurgy supplies about 24% of the entire sulphuric acid produced in the USSR.[12]

The industrial oxidation of sulphur dioxide is achieved in the presence of vanadium catalysts. The active component has a complex composition and one can assume to a first approximation that it consists of potassium sulpho- and pyrosulpho-vanadates dissolved in an excess of potassium pyrosulphovanadate. Under the reaction conditions, the active component is in the fused state on the surface of the solid carrier, usually silica. The liquid state of the active component is a precondition for the occurrence of the reaction in the bulk of the melt after the preliminary dissolution of the gaseous components.[145] The oxidation is as a rule carried out in multichamber reactors with intermediate removal of heat. The sulphur trioxide formed is absorbed to form commercial sulphuric acid. At initial SO_2 concentrations in excess of 5 vol.%, it is useful to employ the double contact method—double absorption, which makes it possible to utilise 99.5–99.9% of the sulphur and to achieve a SO_2 content at the outlet which is the same as after chemical purification, i.e. 0.02–0.05%.[12] The complexity and expense of the manufacture of sulphuric acid are associated with the significant reversibility of the reaction $SO_2 + {}^1/_2O_2 = SO_3$ in the temperature range 400–600 °C, where vanadium catalysts exhibit an acceptable activity.

In order to obtain sulphuric acid from gases in which the SO_2 concentration is less than 3–3.5% in multichamber apparatus, it is necessary either to heat the gases continuously to 400–450 °C or to "fortify" the dilute gas with sulphur dioxide obtained by combusting sulphur in a stream of air[182] or by the effluent gases from autogenic processes containing more than 11 vol.% of SO_2.[183]

The catalytic oxidation of SO_2 in a non-stationary regime in the presence of the traditional vanadium catalyst significantly simplifies the process and lowers its cost.[178,184] This method makes it possible to reduce the amount of metal required for the catalytic unit by a factor of 1.5–5, to decrease the hydraulic resistance by a factor of 1.5–2, to diminish the total capital cost by 30–80%, and to reduce the intrinsic cost of sulphuric acid by 5–20% compared with the existing method. It does not require the consumption of fuel for heating the mixture in the processing of gases containing more than 0.6% of SO_2, while in the presence of more than 4–5% of the dioxide additional heat can be obtained.

A characteristic feature of the non-stationary method for the oxidation of SO_2 to SO_3 is the appearance along the length of the catalyst bed of a region where the temperature decreases (Fig. 2). This gives rise to the possibility of achieving a temperature regime close to one which is theoretically optimal for irreversible exothermic processes, makes it possible to reduce the number of catalyst layers, and virtually obviates the need for intermediate heat exchangers in an industrial reactor. The use of industrial reactors[185–197] operating under periodic mixture reversal conditions showed that they can be readily regulated, permit a stable processing of gases in which the concentration of sulphur dioxide varies by an order of magnitude, and retain their working temperatures when the process is arrested even for several days. It is noteworthy that, at initial sulphur dioxide concentrations less than 2.5–3%, it is possible to achieve a degree of conversion of SO_2 into SO_3 of 97–98% on a single-bed reactor. The technical characteristics of one of the industrial catalytic types of apparatus for the oxidation of SO_2 to SO_3 on the basis of the reversal process are presented in Table 1. In terms of technological parameters (degree of purification, maximum temperatures), the experimental data obtained on industrial apparatus agree satisfactorily with the values calculated on the basis of mathematical models for non-stationary processes.[148]

(c) Hydrogen sulphide

The hydrogen sulphide contained in acid gases resulting from the processing of petroleum and natural gas is one of the main sources of sulphur.[188] The Claus process is usually employed to extract sulphur. In this method, the gas containing predominantly hydrogen sulphide and carbon dioxide is oxidised at high temperatures in a Claus furnace by air or oxygen with formation of elemental sulphur, sulphur dioxide, and also a certain amount of COS and CS_2. Air (or oxygen) is supplied in an amount such that the concentration ratio $H_2S:SO_2 = 2$ is ensured at the outlet from the furnace. The degree of conversion of hydrogen sulphide into sulphur reaches 60–70%. Next, the mixture is cooled, condensed, and the sulphur is separated, while the gases are subjected to catalytic conversion using active alumina, bauxites, titanium dioxide, etc. as catalysts.[189,190] The reversible exothermic reaction $2H_2S + SO_2 = 3S + 2H_2O$ takes place on the catalyst. The equilibrium degree of conversion increases rapidly with decrease in temperature. However, at low temperatures, the sulphur formed condenses, blocking and thereby deactivating the catalyst. The process is therefore performed in several catalytic stages with the intermediate cooling and separation of sulphur.

A degree of extraction of sulphur up to 96% (overall degree of extraction including the degree of extraction of sulphur in the Claus surface) is attained in the two-stage process, while in the three-stage process the degree of extraction is up to 98%. In order to attain higher parameters, different fairly expensive processes for the additional purification of residual gases are used: afterburning, including catalytic afterburning, to give SO_2 with subsequent processing or ejection to the atmosphere; hydrogenation to H_2S with subsequent conversion into sulphur; preparation of sulphur by the Claus method but under specific conditions.[191–195] Schemes involving "dry" additional purification of gases, based on carrying out the Claus reaction at temperatures below the dew point of the sulphur formed, have come to be most widely used.[191] The process is usually carried out as follows. The reaction is performed at 120–135 °C, which ensures a high degree of conversion, but the sulphur formed is condensed in the pores of the catalyst (alumina). After the saturation of the bed, the catalyst is regenerated at 300–350 °C, the regeneration being accompanied by the evolution and subsequent condensation of sulphur. In order to ensure the continuity of the process, it is carried out in several parallel reactors, each of which operates in succession under catalytic conditions—adsorption of sulphur, regeneration, and cooling. By 1986, about 70 industrial plants with "dry" additional purification, ensuring an average extraction of H_2S of 99–99.5%, operated throughout the world.[191]

The actively developing liquid-phase methods for the additional purification of the residual gases from the Claus process are an alternative to the "dry" methods,[191-193] but their wide scale industrial application is prevented by the high capital costs, the formation of acid waste, and the low quality of the sulphur formed.[194]

The non-stationary method for the manufacture of sulphur on the basis of the Claus method in a stationary catalyst bed under periodic mixture reversal conditions[196,197] makes it possible to reduce greatly the capital and energy (operating) expenditure.

The process is carried out as follows. The initial gas mixture at a low temperature (120–116 °C) is supplied to the catalyst bed, which was heated beforehand. The sulphur formed then condenses in the reaction zone suppressing the activity of the catalyst until its complete deactivation. After the introduction of the mixture into a "fresh" bed, the initial sections of the bed are gradually deactivated and the reaction zone slowly shifts into the bulk of the bed in the direction of the filtration of the gas. A moving "sulphur condensation front" is thus produced together with the temperature and concentration fronts associated with it. After a certain time, the direction of motion of the reaction mixture is reversed. An analogous condensation front then begins to move from the opposite side and the previously condensed sulphur vaporises as a result of the heat of reaction. The use of various modifications of the Claus flow reversal process makes it possible to achieve a degree of elimination of H_2S from the gas above 99%.

It is sometimes desirable to utilise the sulphur dioxide from sulphur-rich gases in the form of elemental sulphur.[188-190] For this purpose, SO_2 is subjected to thermal reduction by various reductants (carbon, CO, CH_4, H_2, hydrocarbons), after which the catalytic Claus reaction between SO_2 and H_2S is carried out. The SO_2 is reduced both using solid catalysts[198] and a non-catalytic procedure in a homogeneous phase.[199]

The utilisation of SO_2 from metallurgical gases can be achieved by means of the liquid-phase sulphur elimination method developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[200,201] based on the liquid-phase reduction of sulphur dioxide by hydrogen sulphide. The chemical sorbent, recirculating during the process, is an aqueous solution of ammoniacal phosphate salts and a homogeneous catalyst based on soluble silicon or aluminium salts, which significantly accelerate the reduction of SO_2 by hydrogen sulphide compared with other known liquid-phase methods.[201]

(d) Organic compounds

The elimination of organic compounds from gases involves the oxidation of the impurities to carbon dioxide and water. Catalytic methods are widely used to make safe the effluent gases from the manufacture of synthetic fibres,[202-204] the gaseous waste from petroleum processing and petrochemical undertakings,[205,206] the venting gases from painting and drying workshops,[207-209] and in the manufacture of electrotechnical articles.[206,210] The relevant reviews[147,211-214] show that the application of catalytic detoxification methods is expanding continuously.

Both catalysts containing precious metals (Pt, Pd)[215,216] and catalysts based on copper, chromium, cobalt, and iron oxides as well as complex oxide systems (chromites, ferrites, cobaltites, etc.)[213] are used for the catalytic afterburning of toxic impurities. Detailed data about Soviet detoxification catalysts have been published.[217] Depending on the nature of the toxic components in the gases, different catalysts are used.

Not only hydrocarbons and carbon monoxide but also nitrogen-containing[218,219] and halogen-containing organic compounds[220,221] can be trapped from gas mixtures by means of catalytic oxidation. By a successful selection of catalysts and process conditions, nitrogen-containing impurities can be oxidised to elemental nitrogen, CO_2, and water,[218] whilst chlorine-containing impurities can be oxidised to HCl, which is bound by alkali.[221]

The temperature of the gases at the inlet to the catalyst bed, required to ensure high degrees of purification, varies from 160–200 °C in the elimination of formaldehyde from gases on platinum-containing catalysts[206,213] to 400–600 °C in the elimination of isopropylbenzene and bitumen vapour from gases on oxide catalysts.[206]

Catalytic afterburning processes are being improved by creating catalysts capable of propagating the oxidation at low temperatures. For example, catalysts for the oxidation of CO to CO_2 at 30 °C have been proposed.[222] In order to reduce the hydrocarbon oxidation temperature, ozone has been introduced as the oxidant into the gas undergoing purification.[223,224] An adsorption-catalytic method is developing vigorously.[225-228] It consists of the adsorption of toxic compounds (for example, styrene[228]) on various catalysts (zeolite-containing catalysts,[225] copper chromite,[226] and a manganese catalyst[228]) with subsequent oxidation of the impurities on raising the temperature at the inlet.

A two-stage process with the intermediate removal of heat and afterconversion of impurities on a second catalyst bed is used to make safe concentrated gaseous waste.[147,229-232] Different catalysts oxidising different impurities can be used in each stage.

The improvement of catalytic processes also involves an increase in the degree of recovery of heat using heat exchangers with turbulisation of the stream.[233] This makes it possible to increase the degree of recovery of heat to 80–85% and to reduce correspondingly the amount of fuel used.

The elimination of various organic substances and CO from industrial effluent gases under conditions involving the periodic reversal of the flow of mixture through a stationary catalyst bed[234-237] ensures the following features compared with the traditional stationary procedure: (a) a decrease in the capital cost of the building of plants by a factor of 1.5–3; (b) a decrease in the intrinsic cost of the purification of gases by a factor of 1.5–2; (c) the autothermal nature of the process under the conditions of variable and low (on average above 0.5 g m^{-3}) contents of toxic impurities; (d) the generation of potentially highly useful heat in the detoxification of gases containing more than 3 g m^{-3} of toxic impurities, which can also ensure that the detoxification process is economical.

For the purification by the non-stationary method of gases at low concentrations, whereupon the adiabatic heating of the mixture (ΔT_{ad}) on complete conversion of harmful substances into CO_2 and water does not exceed 15 K, it has been suggested[235] that an additional minimum amount of fuel which would ensure, together with the toxic components, the necessary degree of heating be introduced into the gas being purified. Such a process has been developed for the detoxification of the effluent gases from painting and drying workshops.

In contrast to the reversible sulphur dioxide oxidation and Claus reactions, oxidation reactions leading to the removal of organic compounds from gases take place reversibly with formation of water and carbon dioxide. This makes it possible to purify gases under non-stationary conditions at the maximum temperatures without the use of fuel and with the minimum amount of catalysts.

The technical parameters of one of the industrial plants for the elimination of organic compounds from gases are presented in Table 1.

Industrial non-stationary catalytic methods for the elimination of the principal industrial gaseous contaminants (NO_x, SO_2, hydrocarbons) from gases have been developed on the basis of the flow reversal process and applied in industry. The efficiency of the non-stationary method has been confirmed by the vigorous development of studies on these lines both in the USSR and abroad.[238–243]

VIII. Non-catalytic chemical methods

If undesirable impurities are removed from gases as a result of a virtually irreversible chemical reaction, whose role is decisive compared with other processes, then such methods of purification will be referred to as chemical. From this standpoint, the methods for the elimination of SO_2 from effluent gases using lime or limestone, for example, are frequently referred to as absorption methods since the decisive operation involves in this case processes in the absorption scrubber. The chemical purification methods are based primarily on the chemical transformation of toxic compounds into harmless (or less toxic) ones or on the activation of chemical reactions. It is useful to include among them also radiation-chemical methods based on the employment of accelerated electrons.[244–247] In many cases, it is useful to introduce ozone into the gases undergoing purification in order to activate chemical reactions.[162,248,249] Examples of the use of chemical purification methods in industry are presented below.

The elimination of NO_x from gases involves the reduction of the impurities to N_2 and H_2O. The homogeneous reduction of NO_x by ammonia occurs mainly at 900–1000 °C. At higher temperatures, the rate of oxidation of ammonia to nitrogen oxides increases significantly, which lowers the degree of purification. This process has been developed mainly by the American Exon Company.[250] The average degree of elimination of NO_x from gases by this method does not at present exceed 60–70%.[152,251,252] The principal ways of increasing the process efficiency involve the improvement of the systems for the mixing of small amounts of ammonia with hot (900–1000 °C) smoke gases,[253] which makes it possible to raise the degree of purification to 80–90%, and the search for new reductants permitting the expansion of the temperature range in which the process can be carried out.[254] Thus it has been suggested that urea be used for the reduction and that the process be performed at 600–1100 °C.[254]

On exposure to a stream of electrons, chemical reactions in gases are appreciably accelerated. This method is suitable mainly for the elimination of NO_x and SO_2 from the smoke gases generated in thermal electric power stations.[244–247] The stream of smoke gases is initially freed from ash, after which ammonia is supplied and the gas mixture is irradiated. This results in the formation of a mixture of the salts $(NH_4)_2SO_4$ and $(NH_4)_2SO_4.2(NH_4)_2SO_3$ from ammonia, nitrogen oxides, and sulphur. After the separation of the salts (for example, on an electrofilter or on a sleeve filter), the gas is ejected through a smoke tube and the mixture of salts is used as a fertiliser. The output of the largest plant operating in the USA is 32000 $m^3 h^{-1}$. The principal advantages of the method are its simplicity and the absence of secondary contaminants, including waste water. The degree of elimination of NO_x attained is usually 70–90%.[244,245] Various modifications of the methods are being developed: with recycling of the purified gas[255] and with irradiation of the gas in two stages, whereupon most of the radiation dose is absorbed in the first stage.[256] The principal disadvantage of the method is believed to be the considerable energy expenditure. Evidence has recently appeared indicating the possibility of the laser irradiation of the gases undergoing purification.[257] The wavelength is then selected so that the preliminary absorption of radiation by sulphur and nitrogen oxides should entail their dissociation with liberation of elemental sulphur and N_2.

Ozone methods are used to remove the toxic SO_2 and NO_x from smoke gases and to deodorise the gaseous waste in industrial undertakings. The introduction of ozone accelerates the oxidation of NO to NO_2 and of SO_2 to SO_3.[257] After the formation of NO_2 and SO_3, ammonia is introduced into the smoke gases and the mixture of the complex fertilisers formed (ammonium sulphate and nitrates) is isolated. The duration of contact between the gas and ozone necessary for the removal of SO_2 (80–90%) and NO_x (70–80%) is 0.4–0.9 s. The energy expenditure on the purification of gases by the ozone method is estimated as 4–4.5% of the equivalent power output of the energy unit, which is apparently the main cause holding back the industrial application of this method.[249]

The use of ozone to destroy the odour of gaseous waste is based on the oxidative decomposition of substances with an unpleasant smell. In one group of methods, ozone is introduced directly into the gas being purified, whilst in another the gases are washed with water which was ozonised beforehand. The subsequent passage of ozonised gas through a layer of activated charcoal[257–261] or its application to the catalyst[262–264] have also been used. When ozone is introduced and the gas is subsequently passed through the catalyst, the temperature of the conversion of substances such as amines, acetaldehyde, and hydrogen sulphide is reduced to 70–80 °C. Both Pt/Al_2O_3 and copper, cobalt, and iron oxides on a carrier are used as catalysts.[263] The ozone methods for the destruction of odour have been used primarily in the purification of gases evolved in the processing of raw material of animal origin in meat (fat) processing plants.[249] This method has so far been scarcely applied in the USSR.

Either pelleted material (crushed charcoal with added lime) is used for the chemical binding of SO_2 or powdered limestone or dolomite is introduced into carbon dust in the combustion of spray-injected fuel. The use of grains containing added lime with the ratio C : S = 3 : 5 reduces the concentration of sulphur dioxide in smoke gases resulting from the combustion of fuel in grate furnaces by 50–70%.[34] In the combustion of coal dust with added lime, the degree of binding of SO_2 reaches 80%.[30] SO_2 is bound similarly after the introduction of sodium salts and in this case there is a possibility of using lower temperatures (110–150 °C).

Three filters are employed for the subsequent separation of the salts formed. The disadvantages of this method are believed to include the inadequate, in many instances, degree of elimination of SO_2 and the solubility of the salts formed.[1]

The different reactivities (differing by a factor of 5) of different kinds of limestone in relation to SO_2 have not so far been adequately explained.[30]

Chemical methods make it possible to achieve the combined elimination of compounds of different types from gases. An example is provided by the method for the simultaneous removal of sulphur dioxide and hydrocarbons from gases.[265] For this purpose, the gas is passed through a layer of hot limestone at a temperature sufficient for the cracking of the hydrocarbons. Sulphur dioxide is

simultaneously converted into calcium sulphide. The regeneration is carried out with oxygen, which affords elemental sulphur.

IX. Biochemical methods

Biochemical purification methods are based on the ability of microorganisms to decompose and transform various compounds. The substances are decomposed on treatment with enzymes generated by microorganisms in the gases undergoing purification. When the gas composition is frequently altered, the microorganisms are unable to adapt by developing new enzymes and the degree of decomposition of harmful impurities becomes incomplete. Biochemical systems are therefore most suitable for the purification of gases of constant composition.

The biochemical purification of gases is carried out either in biofilters or in bioscrubbers. In biofilters, the gas undergoing purification is passed through a layer of packing irrigated with water, which gives rise to a moisture content sufficient to maintain the vital activity of microorganisms. The surface of the packing is coated with a biologically active biofilm (BF) comprising microorganisms. In the course of their vital activity, the microorganisms of the biofilm absorb and decompose the substances contained in air, which results in the growth of their mass. The efficiency of the purification is determined to a large extent by the mass transfer from the gas phase to the biofilm and by the uniform distribution of the gas in the layer of packing. Filters of this kind are used, for example, to deodorise air.[11,266] In this case, the gas stream undergoing purification is filtered under conditions where its flow is parallel to that of the irrigating liquid containing nutrient substances. Beyond the filter, the liquid enters settling chambers and is then again directed to irrigating units.

At the present time biofilters are already used fairly widely for the removal of ammonia, phenol, cresol, formaldehyde, organic solvents introduced in the painting and drying processes, hydrogen sulphide, methanethiol, and other organosulphur compounds from effluent gases. The degree of purification of effluent gases is 95–99%.[267–269] Under normal operating conditions, complete deodorisation is observed beyond the biofilters as a result of the elimination of compounds with an unpleasant smell, for example, methanethiol and hydrogen sulphide. The hydraulic resistance of biofilters ranges from 250 to 2000 Pa and the average contact time is 10–25 s.[266,267]

Bioscrubbers are absorption devices in which the irrigating liquid (absorbent) is an aqueous suspension of active sludge with microorganisms. The gas being purified is usually supplied to the scrubber from below and passes through a packing in a countercurrent relative to the irrigating absorbent. The decomposition reactions of the trapped impurities occur in the aerator-reactor. In order to maintain the vital activity of the microorganisms, the necessary nutrient substances are continuously introduced into the system. Bioscrubbers have found applications for the purification of effluent gases from metal casting industries containing phenol, formaldehyde, ammonia, hydrocyanic acid, and cracking products[267,270] and also in the elimination of butyl acetate, xylene, and alcohols from painting workshop gases.[266]

The overall content of impurities in the gases to be purified can be 750–800 mg m^{-3}.[266] The productivity of bioscrubbers reaches 300 000 $m^3 h^{-1}$, the contact time does not usually exceed 10 s, and the hydraulic resistance is 1000–1500 Pa. The degree of purification reaches 75–98%.

Further improvement of biochemical gas purification systems involves the intensification of the decomposition reactions of the trapped impurities, which is promoted by the injection of highly dispersed activated charcoal into the irrigating liquid.[271] In this case, the microorganisms are adsorbed on the large internal surface of the charcoal.[272–274] Attempts have been made to intensify the biochemical purification by applying electric fields to the system containing the activated charcoal.[275]

The development of biochemical purification methods has led to the creation of biofilters with an artificially formed structure and a specially grown biofilm. The linear flow rates of the gases being purified in such systems can reach 0.5–1.0 m s^{-1}, which is higher by a factor of 80 than in processes involving the use of natural materials. The largest biofilters of this type are being used in the Federal Republic of Germany (70 000 $m^3 h^{-1}$).[276] This procedure is most applicable to the purification of gases with a low concentration of impurities. Polymeric materials [polyethylene, poly(vinyl chloride)] are widely used in bioscrubbers. Apart from the Federal Republic of Germany, the biochemical gas purification method has found practical applications in Japan.[266,277–279] Biological gas purification methods have been recommended for the deodorisation of the effluent gases from veterinary-sanitary product factories, food processing undertakings, sewage processing plants, etc.[277]

X. Conclusion

A large number of different methods for the removal of the principal contaminants (NO_x, SO_2, H_2S, carbon monoxide, and various organic substances) from gases have now been developed and tested in industry. We shall indicate the principal applications of these methods and their present state. The absorption methods are used mainly to trap acid components from gaseous waste (SO_2, H_2S, HCl, SO_3, NO_x, NH_3, etc.). In many cases, this makes it possible to obtain useful products—acids and salts. This method is used in practice much more rarely for the removal of hydrocarbons from gases, which is caused primarily by the high cost of absorbents. The principal disadvantages of absorption methods are the formation of liquid waste and the cumbersome apparatus used.

The adsorption methods are some of the most widely used industrial procedures for the purification of gases. Their application makes it possible to return to industry many valuable compounds. At impurity concentrations in the gases more than 2–5 g m^{-3}, the purification is actually profitable. The principal disadvantage of the adsorption method is the large energy consumption in the desorption and subsequent separation stages, which greatly complicates its application to the purification of multicomponent mixtures.

Thermal methods are widely used to eliminate toxic combustible compounds from effluent gases. The afterburning plants developed in recent years are distinguished by their compactness and low energy expenditure. The application of thermal methods is effective for the afterburning of multicomponent and dust-saturated effluent gases.

The principal aspects of the development of catalytic methods are the creation of cheap catalysts operating effectively at low temperatures and resistant to various poisons as well as the development of energy saving technological processes with low capital costs for equipment. Catalytic methods have found the largest-scale application in the elimination of nitrogen oxides from gases, in the detoxification and utilisation of a wide variety of

sulphur compounds, and in the detoxification of organic compounds and CO.

Condensation methods are used on an industrial scale normally in the presence of high concentrations of the impurities to be trapped. In order to attain the necessary degree of purification after condensation, it is as a rule essential to employ some other methods, for example, catalytic methods.

The development of chemical methods is associated with the search for effective procedures for the activation of chemical gas-purification reactions. Methods involving the homogeneous reduction of NO_x and ozone methods for the deodorisation of compounds with an unpleasant smell found fairly extensive industrial applications.

The experience gained in the prolonged use of biochemical plants and the simplicity of their technical operation and the apparatus involved make it possible to recommend this procedure for extensive application, primarily for the elimination of organic compounds from gaseous waste with low concentrations of impurities. Among the disadvantages of biochemical methods, one should include, firstly, the low rate of biochemical reactions, which increases the size of the equipment, secondly, the specificity (high selectivity) of the strains of microorganisms, which hinders the processing of multicomponent mixtures, and, thirdly, the difficulty of processing variable-composition mixtures.

The industrial application of membrane methods is being held back so far by the low specific productivity of membranes, the low degree of purification, the necessity to generate a high excess pressure, the large size of the equipment, and the large capital and operating costs.

The improvement of traditional purification methods (adsorption, absorption, thermal afterburning, and condensation) and the development of new ones (catalytic, membrane, chemical, and biochemical) tend to reduce the capital and operating costs (mainly energy expenditure) involved in their application. In most cases, the problems associated with the purification of effluent gases can be solved in different ways. For example, solvents can be removed from gases with the aid of adsorption, by thermal and catalytic oxidation, and by biochemical and absorption methods, each procedure permitting the attainment of virtually any degree of purification. In every specific case, the choice of the detoxification method is an economic problem. There are no poor and good methods. There are only expensive and cheap ones.

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Heterogeneous processes in the Earth's atmosphere and their ecological consequences†

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ABSTRACT. The principal information about the heterogeneous reactions involving ozone and other minor constituents of the atmosphere is described. The influence of the simplest heterogeneous reactions on the gas composition of the atmosphere in the middle latitudes and on tropospheric stratospheric coupling is examined on the basis of model estimates. The real situations and certain scenarios for an appreciable improvement of the gas composition of the atmosphere as a result of heterogeneous reactions are analysed. The oxidation of sulphate ions in cloud droplets is considered.

The bibliography includes 105 references.

Contents

I.	Introduction	1007
II.	Brief information about atmospheric aerosols	1007
III.	The influence of heterogeneous reactions on the concentrations of ozone and other minor constituents of the atmosphere	1009
IV.	Chemical reactions in cloud drops	1016

I. Introduction

The heterogenous chemical processes in the atmosphere have been attracting an increasing amount of attention.[1] The interest in this field of chemistry has intensified especially during recent years in connection with the appearance of ideas about the effective influence of heterogeneous reactions on the decomposition of the ozone layer in the Antarctic during spring.

For ecology, three problems associated with heterogeneous chemical phenomena in the atmosphere are of greatest importance; (1) the change in the gas composition under the influence of heterogeneous processes; (2) dissolution and reactions in drops leading to acid rain; (3) chemical formation and growth of aerosols. Attention will be concentrated on the first two problems in this review. We shall endeavour to base the review on specific examples, concentrating attention on the problem of the content of ozone and hydroxyl radicals in the atmosphere and the problem of acid rain. The results of laboratory studies on the interaction of atmospheric gases with the surfaces of solids and liquids whose compositions are similar to those of atmospheric aerosols are also represented although without a detailed analysis.

† The five articles at the beginning of this issue are a continuation of issue No. 10 devoted to the "chemistry of the atmosphere".

The problem of the influence of changes in the radiation balance and in the intensity of the solar radiation passing through the atmosphere on the composition of the latter are outside the scope of this review. As a rule, we shall consider the situations in which the chemical action of aerosol particles on the gas composition of the atmosphere is more effective than the optical or thermochemical influences.

II. Brief information about atmospheric aerosols

1. Chemical composition

Primary aerosol particles appear in the atmosphere as a result of soil erosion, while in the layer near the water over the oceans there are salt particles. Anthropogenic sources also make an appreciable and increasing contribution. Secondary aerosols are formed in the atmosphere itself as a result of the chemical reactions of gases of natural and anthropogenic origin. The commonest of these are sulphuric acid particles — the principal aerosols of the stratosphere. It is believed that sulphuric acid is formed as a result of the photochemical transformation of carbon oxide sulphide COS into sulphur dioxide and the subsequent oxidation of the latter to H_2SO_4.[2,3] The chemical homogeneity and a single-peaked distribution of the particles with respect to size throughout the middle latitudes may serve as confirmation of a unique mechanism for the formation of the stratospheric sulphuric acid aerosol. In the troposphere, where COS is not photolysed and does not react with atomic oxygen, the formation of sulphuric acid particles is due to the chemical reactions of the SO_2 molecules arriving from the earth. Review information about the mechanisms of the formation of secondary aerosols is available in monographs.[2–5]

In the aerosol model of photochemical reactions, it is postulated that under normal (background) conditions the particles of the troposphere have the following composition[6]: up to a height of 3 km — 50% of sulphates (the main form is ammonium sulphate), 35% of soil particles, and 15% of sea salt (NaCl); above 3 km — 60% of sulphates and 40% of soil particles. According to this model, the soil particles consist of 53% SiO_2, 17% Al_2O_3, 7% of Fe_2O_3, and 23% of other compounds. The chemical composition of the aerosols in industrial regions may be different. For example, the aerosol over Houston (USA) consists of sulphuric acid to the extent of 30%[7], and in certain cases the H_2SO_4 content in aerosol over cities may reach 50%[2]. In city aerosols the fraction of SiO_2 may be 30%, while the contribution of aluminium oxide is up to 10% and that of iron oxides is several per cent[2]. In extreme situations (large amounts of industrial waste, forest fires, volcanic eruptions, nuclear explosions), the composition and concentration of aerosol particles

may change significantly. More detailed information about the physicochemical properties of aerosols is available in other publications [1,2,8].

As already stated, the stratospheric aerosol in the middle latitudes consists under background conditions mainly of sulphuric acid particles (the Junge layer, height $Z = 18-20$ km). Immediately after volcanic eruptions, a large amount of sulphur compounds and particles of volcanic ash penetrate into the lower layers of the stratosphere. These have the following approximate composition: 60% SiO_2, 20% Al_2O_3, 3% Fe_2O_3, 2% MgO, 5% CaO, 5% Na_2O. The primary volcanic stratospheric aerosol particles are apparently to a large extent coated by sulphuric acid and water. As a result of chemical reactions involving the sulphur compounds H_2S and SO_2, ejected in volcanic eruptions to a height of 25–30 km, aqueous sulphuric acid aerosols, containing between 60 and 80% of H_2SO_4, are produced. They then fall downwards and concentrate in the lower part of the stratosphere at a height of 18–20 km.

The composition of the stratospheric polar clouds, formed during the winter in the Arctic and the Antarctic, is more homogeneous. These are mainly ice particles with dissolved nitric and hydrochloric acid molecules [9,10]. The ice particles and water drops are the natural constituents of the stratospheric and tropospheric aerosols.

2. The size, distribution with respect to height and the number concentration of particles

Tropospheric aerosols can be subdivided according to particle size into three characteristic ranges (modes) [2,11,12]. The first mode consists of condensation nuclei which are particles with a radius less than 0.2 μm, the second mode comprises growing particles with a radius of 0.2–1 μm, and the third mode includes particles with a radius from 1 to 10 μm. The concentration of the solid non-hydrated particles constituting the first mode in the troposphere is highest and the main bulk of the surface of the solid particles per unit volume (the specific surface A) actually corresponds to them. The average particle radius which contributes most A is 0.13 μm [2]. The growing particles of the second mode are as a rule non-uniform in composition and appreciable amounts of water may be present on their surfaces. Large particles ($r > 1$ μm) are mainly highly hydrated forms or water drops.

The distribution of the concentration of solid particles in the troposphere with respect to height can be conveniently represented in an exponential form:

$$N_Z = N_0 e^{-Z/Z_0}. \quad (1)$$

The concentration N_0 at the Earth's surface and the characteristic height Z_0 depend on specific conditions (region, temperature, humidity). The following model is available for the distribution of aerosol particles of the troposphere with respect to height [2]: first mode—$N_0 = 10^3-10^5$ cm^{-3}, $Z_0 = 2-3$ km; second mode—$N_0 = 5-300$ cm^{-3}, $Z_0 = 1.5-2$ km; third mode—$N_0 = 10^{-2}-10^{-4}$ cm^{-3}, $Z_0 = 0.5-1$ km. The stratospheric aerosol in the middle latitudes is located at a height of 16–22 km (the Junge layer). The concentration of sulphuric acid particles is a maximum at a height of 18–20 km and their average radius is 0.05–0.1 μm. During volcanic eruptions, the concentration of aerosol particles in the stratosphere increases by a factor of 20–30, approaching the background concentration of aerosols near the Earth's surface ($\sim 10^3$ cm^{-3}).

The specific aerosol surface A in the troposhere near the Earth's surface under normal conditions, in volcanic clouds [13], and also in cold polar stratospheric clouds [9,10,14] is approximately the same and amounts to 10–50 μm^2 and cm^{-3} or $(1-5) \times 10^{-7}$ cm^{-1}. The polar stratospheric clouds are concentrated in regions with a temperature below −85 °C [15]. In the cold Antarctic stratosphere, the maximum density of aerosol particles is attained at a height of 16–18 km and there are several sharp concentration peaks in this region.[16]

3. The rate constant for a heterogeneous reaction

The interaction of molecules with the surface includes a series of stages: adsorption and desorption, diffusion within the liquid aerosol and evaporation, and reactions of the adsorbed molecules with one another and with the molecules of the adsorbent or the molecules incident from the gas phase. The probability of the reactions γ depends both on the parameters of the atmosphere (temperature, pressure, humidity) and on its gas composition. Furthermore, the chemical composition of the aerosols themselves is a function of the state of the atmosphere. This gives rise to considerable complications as regards a self-consistent description of the composition of the atmosphere taking into account its multiphase nature and the presence of definite relations between the heterogeneous and homogeneous phases (see, for example, Carmichael et al.[17]). In view of the complexity of the problem, the heterogeneous fraction is parametrised by specifying the average particle size r, the concentration of aerosol particles N, and the reaction probability γ or by introducing the specific surface A and γ. The parameters r, N, and A are determined from the results of experiments under natural conditions and the values of γ are based on laboratory data.

The rate of consumption of gases in a reaction involving spherical atmospheric particles is described by the equation for a unimolecular first-order process with an effective rate constant [18] given by

$$K_{het} = \frac{4\pi r N D}{1 + \lambda l/r}, \quad (2)$$

where D is the molecular diffusion coefficient, l the length of the free path in the gas, and

$$\lambda(\gamma) = \lambda_{\gamma=1} + \frac{4(1-\gamma)}{3\gamma}. \quad (3)$$

Here $\lambda_{(\gamma=1)} \simeq 1$ is a function weakly dependent on the Knudsen number $K_n = l/r$. The value of the function varies from 0.71 to 1.3 as l/r varies from 0 to ∞. At atmospheric pressure, $l \simeq 0.1$ μm, which is close to the radius of the solid tropospheric particles making the main contribution to the specific surface and the parameter $\gamma l/r$ almost always exceeds unity. Only a small region of the atmosphere near the Earth's surface, where $\lambda l/r$ is close to unity for $\gamma \simeq 1$, is an exception. Therefore, under atmospheric conditions, the limiting case of the destruction of molecules on solid particles in the kinetic region, where $\lambda l r \gg 1$, occurs most widely. In this case, the heterogeneous consumption constant is

$$K_{het} \simeq \frac{c\gamma}{4} A, \quad (4)$$

where c is the average thermal velocity of the molecules (it is assumed that $D = lc/3$. Eqn. (4) yields the number of active collisions of the molecules with the surface, per unit volume, in 1 s. The approximate form of the dependences of A on the height [8,19] is illustrated in Fig. 1. The values of A in the background atmosphere near the Earth's surface (~ 100 μm^3 cm^{-3}) and in volcanic and polar clouds (10–50 μm^2 cm^{-3}) are approximately the same. In urbanised regions, A at the Earth's surface is higher by two orders of

magnitude than the background value, while in the Junge layer under background conditions $A \simeq 1$ μm^2 cm^{-3}. The values of γ required for the calculation of K_{het} are presented below.

III. The influence of heterogeneous reactions on the concentrations of ozone and other minor constituents of the atmosphere

1. Model estimates for the atmosphere in the middle latitudes

Together with oxygen and nitrogen, the atmosphere contains many other constitutes at a low concentration (the so called minor constituents). These comprise primarily the gases H_2O, CH_4, N_2O, NO_x, etc. ariving from the Earth and entering into various reactions, the reservoir gases H_2O_2, N_2O_5, HNO_3, HCl, HOCl, $ClONO_2$, HO_2NO_2, etc. formed in photochemical reactions, as well as the radicals H, OH, HO_2, $O(^3P)$, $O(^1D)$, NO, NO_2, Cl, ClO, etc. In the modelling of the minor constituents, all the gases are divided into families[3]. The oxygen family includes $O(^1D)$, $O(^3P)$, and O_3. The active odd hydrogen family comprises the H, OH, and HO_2 radical species. The OH and HO_2 radicals play a decisive role in establishing the gas composition of the stratosphere and especially the troposphere. Their concentration depends to a large extent on the content of hydrogen peroxide, which is the principal reservoir of the hydrogen family and supplies OH radicals by its photolysis. The odd nitrogen family $NO_x = NO + NO_2$ is closely related to the NO_y family, which incorporates the reservoir gases N_2O_5, HNO_3, $ClONO_2$, and HO_2NO_2, whose photolysis leads to the formation of NO_2. The calculated and experimental concentrations of many gas constituents have been published in monogrphs[3,4] and in a review[8]. The heterogeneous decomposition of long-lived components of the atmosphere, whose chemical reactions are slower than their vertical transport, must be taken into account for $\tau_{het} \lesssim 10\tau_D$, where $\tau_{het} = K_{het}^{-1}$ and $\tau_D = H^2/K$ are respectively the characteristic heterogeneous decomposition and vertical transport times. The height of the uniform atmosphere $H = 5-7$ km and the turbulent transport (eddy diffusion) coefficient $K \simeq (10^4-10^5)$ cm^2 s^{-1}. The contribution of heterogeneous decomposition is appreciable if

$$\gamma > \frac{0.4K}{cH^2A} \simeq \frac{(10^{-12}-10^{-13})}{A} \text{ cm}^{-1}. \quad (5)$$

A specific surface $A \simeq 10^{-7}-10^{-6}$ cm^{-1} is characteristic of the background troposphere near the Earth's surface and stratospheric clouds (see Fig. 1) and heterogeneous processes must therefore be taken into account if

$$\gamma_1 > 10^{-7}-10^{-5}. \quad (6)$$

Over highly polluted cities, A reaches $10^{-4}-10^{-5}$ cm^{-1} and heterogeneous reactions may prove to be significant already when

$$\gamma_2 > 10^{-9}-10^{-7}. \quad (7)$$

The long-lived components of the atmosphere include methane, N_2O, and fully substituted chlorofluorocarbons (Freons). Generally speaking, low values of γ such as $10^{-9}-10^{-7}$ may be entirely realistic characteristics of the catalytic oxidation of methane, for example, on the surfaces of the oxides Al_2O_3 and Fe_2O_3, or of the heterogeneous decomposition of N_2O. However, there is apparently no direct evidence for the occurrence of heterogeneous-catalytic reactions in the atmosphere.

It is more difficult to select a criterion of the need to include heterogeneous reactions when one is dealing with chemically reactive gases whose lifetime is shorter than the vertical or horizontal transport time. This applies primarily to radicals. For example, the rate of the heterogeneous destruction of the OH or HO_2 radicals must be compared with the rate of descent of these radicals and reservoir gases, in which they are "stored". In particular, the main radical destruction processes of the radicals of the hydrogen family, OH and HO_2, in the troposphere are the reaction $\dot{O}H + H_2O_2 \rightarrow H_2O$ and $H\dot{O}_2$ and the heterogeneous elution of hydrogen peroxide. Their overall rate at the surface of the Earth is $W \simeq 10^5$ cm^{-3} s^{-1} [8,20-22]. With increase in height, the rate of destruction falls.

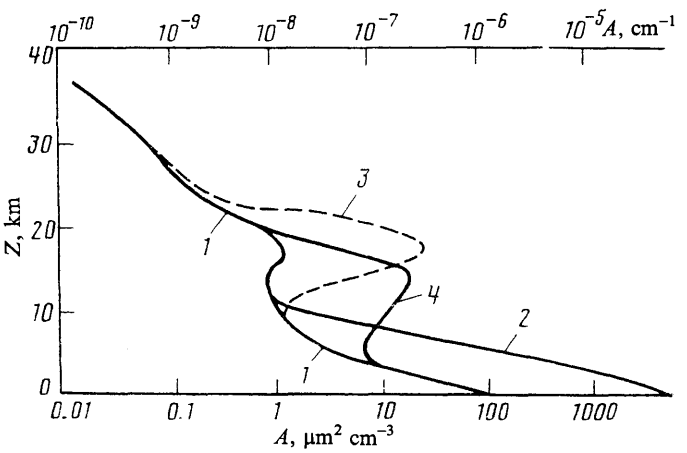


Figure 1. An approximate illustration of the distribution of the specific aerosol surface[19,20]: *1*, background atmosphere; *2*, urbanised regions; *3*, stratospheric volcanic clouds; *4*, polar stratospheric clouds.

The aerosol decomposition of OH or HO_2 must be taken into account when

$$W_A = K_{het}[R] > 0.1W \quad (8)$$

or

$$\gamma \geq \frac{0.4W}{c[R]}. \quad (9)$$

Here $[R]$ is the concentration of radicals. At the Earth's surface, [OH] $\simeq 10^6$ cm^{-3}, [HO_2] $\simeq 10^8$ cm^{-3} [8,22], and condition (9) assumes the form

$$\gamma_{OH} > \frac{10^{-6} \text{ cm}^{-1}}{A} \text{ and } \gamma_{HO_2} > \frac{10^{-8} \text{ cm}^{-1}}{A}. \quad (10)$$

Fig. 1 makes it possible to trace the range of values of γ for which it is necessary to take into account the heterogeneous destruction of OH and HO_2. Under background conditions, $\gamma_{OH} \simeq 0.3-1$ and $\gamma_{HO_2} \gtrsim 10^{-2}$. For polluted cities, the estimates are displaced by two orders of magnitude: $\gamma_{OH} \gtrsim 10^{-2}$ and $\gamma_{HO_2} \gtrsim 10^{-4}$.

Probable estimates for heterogeneous O_3, NO_x, and HO_x decomposition processes on aerosols, carried out in accordance with different models, have been published in a review.[8] In the

calculations based on the one-dimensional model, use was made of the average specific surface of the aerosol (20 μm^{-2} cm^{-3}), which does not vary along the height and corresponds to the particle content in the background atmosphere and also in the stratospheric volcanic and polar clouds. The hypothesis that the specific surface profile is constant as a function of height makes it possible to estimate the sensitivity of the atmosphere to the aerosol decomposition of various compounds in the troposphere and the stratosphere. Direct heterogeneous decomposition of ozone affects its content and the concentrations of other minor constituents (NO_x, HO_x) for $\gamma_{O_3} \gtrsim 10^{-4}$ and the process is most significant at a height of 18–20 km, i.e. at the height corresponding to the stratification of volcanic clouds. The direct decomposition of ozone leads to concomitant changes in the concentrations of other minor constitutents. In the stratosphere, where the homogeneous decomposition of O_3 is mainly caused by the reactions of the nitrogen cycle

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \ , \\ \underline{NO_2 + O} &\underline{\rightarrow NO + O_2} \ , \\ O + O_3 &\rightarrow 2O_2 \ , \end{aligned}$$

the decrease in $[O_3]$ leads to an increase in the NO and NO_2 concentrations, while in the troposphere, where the destruction of ozone is associated with the reactions of the hydrogen cycle

$$\begin{aligned} OH + O_3 &\rightarrow HO_2 + O_2 \ , \\ \underline{HO_2 + O_3} &\underline{\rightarrow OH + 2O_2} \ , \\ 2O_3 &\rightarrow 3O_2 \ , \end{aligned}$$

the concentration of gases of the given family increases.

The critical value of γ_{NO_x}, beyond which the gas composition diminishes owing to the capture of NO and NO_2 by the aerosol surface, is 10^{-5}. However, for $\gamma_{NO_x} \simeq 10^{-5}$, large changes in concentration occur only in the upper stratosphere ($Z > 30$ km), where the specific surface of the aerosols apparently never reaches the value 20 μm^2 cm^{-3} adopted in the model under consideration. It is of interest that the presence of the stratospheric-tropospheric coupling leads to an increase in the amount of NO_x in the troposphere even if there is an additional heterogeneous NO_x sink. This is associated with the fact that the additional destruction of NO_x in the stratosphere induces a marked increase in the content of stratospheric ozone and a decrease in the intensity of the radiation penetrating the troposphere. This diminishes the rate of photodissociation of O_3 $[O_3 + h\nu \rightarrow O(^1D) + O_2]$ and the rate of the main OH radical formation reaction in the troposphere $O(^1D) + H_2O \rightarrow 2OH$. The decrease in the concentration of the tropospheric hydroxyls as a result of the heterogeneous destruction of NO_x in the stratosphere decreases the rate of removal of NO_x via the principal homogeneous reaction $\dot{O}H + NO_2 + M \rightarrow HNO_3 + M$. The contribution of this process, which exceeds the contribution of the direct heterogeneous destruction of NO_x in the troposphere, becomes increasingly significant with increase in γ_{NO_x}.

The critical values of γ_{OH} and γ_{HO_2} under the conditions near the Earth's surface were given above. For a uniform distribution of the aerosol with $A = 20$ μm^2 cm^{-3}, the contribution of the heterogeneous OH destruction to the change in the composition of the atmosphere should be higher than for the background distribution.

The influences of the heterogeneous destruction of the hydrogen family radicals OH and HO_2 on the content of tropospheric and stratospheric ozone are qualitatively different. In the troposphere, where O_3 is decomposed mainly in the hydrogen cycle, the additional decrease in the OH and HO_2 concentrations entails an increase in the ozone content, while in the stratosphere an increase in the NO_x concentration as a result of the diminution of the OH concentration (the rate of the reaction $\dot{O}H + NO_x + M \rightarrow HONO_x + M$ falls) leads to additional decomposition of O_3 in the nitrogen cycle. The results of modern calculations performed for $\gamma_{OH} = 0.1$ [8] have shown that a decrease in the OH concentration is accompanied by an increase in the NO_x content at all heights. On the other hand, the ozone concentrations in the troposphere and the stratosphere vary in different ways.

2. Laboratory studies on the heterogeneous decomposition of ozone and the $\dot{O}H$ and $H\dot{O}_2$ radicals

The first systematic studies on the heterogeneous interaction of the gases distributed in the atmosphere with substances whose compositions are close to those of the aerosols were carried out in 1979.[23] The interaction of the carbon particles and sulphuric acid drops characteristic of the polluted atmosphere of cities was considered. The reactions on the H_2SO_4 surface at 300 K were studied most thoroughly. For the majority of gases, including O_3, NO, NO_2, alkenes, alkanes, CF_4, CCl_2F_2, and atomic O and N, $\gamma < 10^{-6}$. The results of measurements for other gases, more reactive in relation to H_2SO_4, are presented below:

Molecule	H_2O	NH_3	H_2O_2	OH	HNO_3	N_2O_5	HO_2NO_2	$ClONO_2$
γ	$\sim 2\cdot10^{-3}$	$>10^{-3}$	$7.8\cdot10^{-4}$	$4.9\cdot10^{-4}$	>2 $4\cdot10^{-4}$	$3.8\cdot10^{-5}$	$2.7\cdot10^{-5}$	10^{-5}

The authors[23] reached the important conclusion that the tropospheric sulphuric acid aerosol can alter the gas composition of the atmosphere in polluted cities. However, a quantitative estimate was not made.

Numerous studies have been devoted to the heterogeneous decomposition of ozone. In this respect, the stratospheric aerosols are naturally of principal interest.

The interaction of ozone with various surfaces [ice, HNO_3, SiO_2, soot, NH_4NO_3, $(NH_4)_2SO_4$, NaCl, H_2SO_4] was studied in greater detail recently and fairly numerous measurements of the values of γ_{O_3} were made.[24] For the majority of materials investigated, $\gamma_{O_3} < 10^{-6}$ and, under the conditions of the stratosphere in the middle latitudes, including volcanic clouds, ozone is therefore only slightly subjected to heterogeneous decomposition. Values of γ greater than or approximately equal to 10^{-5} were obtained for the Al_2O_3 [25,26] and soot[24] surfaces. Such surfaces can influence the concentration of stratospheric ozone in certain extreme situations. For example, the scenario of a nuclear explosion in mines, whereupon large amounts of soil basalt can enter the atmosphere, has been considered.[27] When the amount of Al_2O_3 ejected reaches 17%, the column of ozone will diminish as a result of direct heterogeneous decomposition to the extent of 30–40%.

It follows from literature data[24,28,29] that the probability of the heterogeneous decomposition of O_3 on the liquid acid depends greatly on a series of factors difficult to take into account, such as the ratio of H_2SO_4 and H_2O, the presence of impurity Fe^{2+} ions,[29] and the duration of the action of O_3 on the surface. Nevertheless, in all cases the values of γ_{O_3} for H_2SO_4 do not exceed 10^{-6}.

The vigorous investigation of the heterogeneous destruction of $\dot{O}H$ and $H\dot{O}_2$ radicals has been promoted in recent years by the development of highly sensitive methods for their detection. The first study of the destruction of OH radicals on the surface of one of the tropospheric aerosols (carbon) was performed in 1975 [30]. The value

$\gamma_{OH} = 5 \times 10^{-2}$ obtained is sufficiently large for the heterogeneous destruction of OH to be taken into account in the modelling of the composition of the atmosphere in polluted cities. The heterogeneous destruction of $\dot{O}H$ [31,32] and $H\dot{O}_2$ [33–35] in the atmosphere was investigated. Table 1 shows that, in the case of typical atmospheric salt aerosols, γ_{OH} is fairly large, amounting to between 8.5×10^{-3} and 0.24 [31]. High values of γ_{OH} are also characeristic of silicon and metal oxides and especially of ice and sulphuric acid.[32] The value $\gamma_{OH} \simeq 1$ obtained for sulphuric acid[32] differs greatly from the value of 4.9×10^{-4} found in another study[23]. Although in both cases concentrated sulphuric acid was used, the surfaces themselves were apparently different. Gershenzon et al.[32] generated a liquid film on a quartz rod by immersing it in liquid sulphuric acid. Baldwin and Golden[23] poured concentrated sulphuric acid onto the bottom of a chamber directing a stream of radicals onto it. In contrast to the study of Baldwin and Golden[23], where the OH recombination products on the surface (most probably water) together with the unreacted OH radicals were directed to a mass spectrometer in which particles with an atomic weight of 17 were detected, Gershenzon et al.[32] used the direct EPR method for the detection of $\dot{O}H$ radicals. It will be shown below that information about the value of γ_{OH} for interaction with a volcanic sulphuric acid aerosol is of fundamental importance for the understanding of the effect of a decrease in ozone concentration after powerful volcanic eruptions.

Table 1. Probabilities of the heterogeneous destruction of $\dot{O}H$ radicals on aerosol-like surfaces.

Surface	γ	T, K	Refs	Surface	γ	T, K	Refs.
$Pb(NO_3)_2$	0.24 ± 0.12	300	[31]	NH_4NO_3	0.01 ± 0.002	300	[31]
NH_4Cl	0.13 ± 0.03	300	[31]	$(NH_4)_2SO_4$	$(8.5\pm1.7)\cdot10^{-3}$	300	[31]
$Fe(NO_3)_3$—FeO_x	0.4 ± 0.08	300	[31]	H_2SO_4	1	300	[32]
$FeSO_4\cdot H_2O$	0.12 ± 0.03	300	[31]	Ice	0.4	250	[32]
$Zn(NO_3)_2$	0.045 ± 0.02	300	[31]	Fe oxide	0.12 ± 0.08	250—350	[32]
$NaNO_3$	0.036 ± 0.018	300	[31]	Al oxide	0.04 ± 0.02	250—350	[32]
Na_2SO_4	0.018 ± 0.01	300	[31]	SiO_2	$(5.6\pm2)\cdot10^{-3}$	250—350	[32]

Table 2. Probabilities of the heterogeneous destruction of $H\dot{O}_2$ radicals on aerosol-like surfaces.

Surface	SiO_2	NaCl	Ag oxide	Fe oxide	Ni oxide	H_2O
γ	$(1-8)\cdot10^{-3}$	$7.5\cdot10^{-3}$	$1.2\cdot10^{-2}$	$1.7\cdot10^{-2}$	$<10^{-3}$	0.2
Refs.	[33—35]	[34, 35]	[33]	[33]	[33]	[36]

For the vast majority of aerosol materials, the values of γ_{OH} are comparatively high and are in the range from 0.1 to 1, although $\gamma_{OH} \simeq 10^{-2}$ for a series of salts and SiO_2 (Table 1).

Although fairly numerous studies on the destruction of $H\dot{O}_2$ radicals on various surfaces have been carried out in recent years, aerosol surfaces have been investigated comparatively little. It follows from Table 2 that the values of $\gamma_{HO_2} \times 10^{-2}$ may be regarded as typical for tropospheric aerosols. It has been noted[33–35] that γ_{HO_2} depends on the presence of water vapour and hydrocarbons in the gas. However, the main factor determining the value of γ_{HO_2} is nevertheless the material of the surface. The temperature dependence of γ_{HO_2} is as a rule negative[34].

The probability of the mass accommodation of HO_2 on finely dispersed water drops saturated with $LiNO_3$ or NH_4HSO_4 has been measured[36]. The apparatus made it possible to model the behaviour of HO_2 in cloud formations, although the size of the aerosol drops in the experiment (0.05—0.1 μm) was appreciably smaller than the size of the cloud drops. The value $\gamma_{HO_2} = 0.2$ obtained is fairly high, which can influence appreciably our ideas about both the composition of the gas in clouds and mist and about the oxidation processes occurring in the water drops (see Section IV).

There is as yet insufficient information about the heterogeneous OH and HO_2 destruction processes. In particular, it is essential to measure γ_{HO_2} for ice, sulphuric acid, and salts of nitric and sulphuric acids [NH_4NO_3, $(NH_4)_2SO_4$, etc.]. Nevertheless, as suggested in a study by one of the authors[37], it is possible to adopt on the basis of the data in Tables 1 and 2 the typical values $\gamma_{OH} \simeq 0.1-1$ and $\gamma_{HO_2} \simeq 10^{-2}$ for all tropospheric aerosols.

3. The influence of heterogeneous processes on the gas composition of the troposphere and on the tropospheric-stratospheric coupling

In the modern molecular models of the atmosphere, account is taken as a rule of only two heterogeneous processes occurring in the troposphere and on the surface of the Earth. The first is associated with the elution of soluble gases or gases reacting with water ("moist elution") and the second involves the precipitation and decomposition of molecules on a supporting surface ("dry deposition").

(a) Dry deposition, moist elution, and the scattering of sunlight by the cloud cover. Dry deposition occurs when gases are adsorbed on the surfaces of the oceans and dry land, after which the adsorbed gases decompose. The destruction of gases at the boundary of the atmosphere as a result of heterogeneous reactions leads to the appearance of a diffusional flux towards the surface. In the chemistry of the atmosphere, this phenomenon is regarded as the deposition of the entire column of gas at a rate V_{de}. The characteristic rate of deposition of O_3 is 0.02 cm s^{-1} on the snow cover and 0.6 cm s^{-1} on soil[8]. In the solution of the problem of the transfer of the SO_2 impurity, the value $V_{de}^{SO_2} = 0.8$ cm s^{-1} was used[38]. The characteristic time of the vertical deposition of the column of gases

$$\tau_{de} = H/V_{de}' \simeq 10^6 - 10^7 \text{ s}$$

is comparable to the time of the turbulent transport in a homogeneous atmosphere to a height $H = 5-7$ km. Model calculations for the summer and winter deposition of ozone[8] have shown that, with decrease in V_{de} by a factor of 30 (from 0.6 to 0.2 cm s^{-1}), the concentration of O_3 at the surface of the Earth increases during the winter by a factor of approximately two. On the

other hand, at a height of 3–5 km the gas composition of the atmosphere virtually no longer depends on the rate of deposition of O_3.

The moist elution of gases readily soluble in water (with a Henry constant greater than 10^3 mol litre^{-1} atm^{-1}) is usually regarded as a first-order process. The distribution of the rate constants for this process with respect to height is consistent with the results of measurements of the content of the minor constitutents carried out in nature. The rate constants for the elution of many gases with different solubilities (H_2O_2, CH_2O, CH_3OOH, HNO_3, etc.) are believed to be the same. This is apparently a fairly rough approximation. According to Logan[22], the elution constants at different heights are

$$K_z = 2.3 \times 10^{-6} \exp[1.6 - 0.4Z]\ \text{s}^{-1} \text{ for } Z < 4 \text{ km},$$

$$K_z = 2.3 \times 10^{-6}\ \text{s}^{-1} \text{ for } Z > 4 \text{ km}. \quad (11)$$

The H_2O_2 moist elution process is decisive in the balance within the hydrogen family in the troposphere. As already pointed out, the loss of this family occurs principally as a result of the elution of hydrogen peroxide[8]. The results of model calculations[39] of the dependence of the concentrations of the minor constituents on the elution constant have been analysed in a review[8]. Variation of K_Z in the range from 10^{-6} to 10^{-5} alters the calculated values of $[HNO_3]$, $[NO_x]$, and $[HO_x]$ by tens and hundreds per cent. The concentrations of the OH and HO_2 radicals undergo a particularly marked change. Thus, with increase in K_Z from 1.15×10^{-6} to 5×10^{-6} s^{-1}, the concentration of radicals at different heights falls by a factor of 1.5–2. Together with the heterogeneous-chemical factors examined above, the gas composition of the troposphere is also affected by the scattering of the solar radiation by cloud drops.

Radicals of the hydrogen family are generated in the troposphere mainly as a result of the reaction $O(^1D) + H_2O \rightarrow 2OH$ and the photolysis of formaldehyde $H_2CO + h\nu \rightarrow H + HCO$. The $O(^1D)$ atoms in the troposphere also appear as a result of photolysis: $O_3 + h\nu \rightarrow O(^1D) + O_2$. The rate of generation of HO_x radicals in the lower troposphere therefore depends markedly on the cloud cover, which scatters solar radiation.

(b) The influence of the heterogeneous destruction of the OH and HO_2 radicals on aerosols on the concentration of tropospheric hydroxyl radicals and other minor constituents of the atmosphere. Under background conditions, one cannot expect appreciable variations in the concentration of hydroxyl radicals as a result of the heterogeneous destruction of OH or HO_2. The destruction of OH and HO_2 radicals on aerosols becomes the main cause of the loss of gases of the hydrogen family in urbanised regions, while the specific aerosol surface increases by more than two orders of magnitude compared with the background value. The gas composition of air over polluted cities has been modelled[38]. The results of one of the calculations of the deviations of the height profiles of the O_3, CO, NO_x, $\dot{O}H$, $H\dot{O}_2$, and H_2O_2 concentrations are presented in Fig. 2. The calculations were performed for $\gamma_{OH} = 1$ and the height profile of the distribution of the aerosol concentration was specified by Eqn. (1), where $N_0 = 10^4$ cm^{-3} and $Z_0 = 1$ km. The average radius of the aerosol particles was assumed to be 0.1 μm. According to theoretical calculations[40] and experimental measurements,[32] the diffusion coefficient of the OH radicals is

$$D_{OH} = \frac{1.41 \cdot 10^{-2} T^{1.72}}{p}\ \text{cm}^2\ \text{s}^{-1}, \quad (12)$$

the pressure p being expressed in mmHg.

Fig. 2 illustrates the percentage deviations of the concentrations of various substituents according to the aerosol model from the concentrations calculated in accordance with the molecular model:

$$\alpha = \frac{[n]_A - [n]_M}{[n]_M}. \quad (13)$$

Fig. 2 shows that the gas composition of the atmosphere in the presence of the aerosol is appreciably modified: the calculated content of the NO_x, CO, and O_3 gases, which are harmful to animals and plants, increases. Furthermore, the content of hydroxyl and perhydroxyl radicals falls by a factor of approximately 4–5. The effect becomes even greater if account is taken of the heterogeneous destruction of HO_2 radicals. For $\gamma_{HO_2} \simeq 10^{-2}$, the concentration of OH radicals near the Earth's surface by a factor of approximately five and that of HO_2 diminishes by a factor greater than 10.

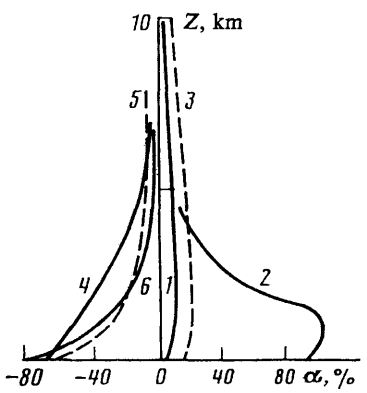


Figure 2. The height profiles of the deviations of the concentration of minor constituents in urbanised regions[38]: *1*, O_3; *2*, NO_2; *3*, CO; *4*, H_2O_2; *5*, $\dot{O}H$; *6*, $H\dot{O}_2$.

(c) The influence of tropospheric heterogeneous processes on the concentration of stratospheric ozone and the oxidation of Freons. OH radicals are known to be the "cleaners" of the atmosphere, ensuring the oxidation of the impurities arriving from the Earth. The self-cleaning of the atmosphere takes place mainly in the lower part of the troposphere, because the temperature and hence the rate of the reactions of OH with impurities decrease with increase in height. We saw above that a number of heterogeneous processes affect the concentration of OH radicals: (1) the scattering of radiation by the cloud cover; (2) dry deposition of O_3; (3) moist elution of H_2O_2; (4) heterogeneous destruction of OH and HO_2 radicals on aerosols. Incomplete allowance for these factors leads to considerable uncertainty in the determination of the concentration of OH radicals. We shall consider in that way this can affect predictions concerning the ozone layer of the atmosphere. The

desruptive effect of Freons is associated with the fact that they do not react with the tropospheric radicals but penetrate freely into the stratosphere. The photodissociation of Freons in the stratosphere leads to the formation of Cl and the decomposition of O_3 in the chlorine cycle:

$$\begin{aligned} &Cl + O_3 \rightarrow ClO + O_2 \ , \\ &\underline{ClO + O \rightarrow Cl + O_2 \ ,} \\ &O + O_3 \rightarrow 2O_2 \ , \end{aligned}$$

The increase in the rate of destruction of the ozone layer associated with the growing manufacture of chlorofluorocarbons, predicted at the present time, can be arrested if an alternative to the Freons can be found[41]. The manufacture of fully halogenated Freons has been prohibited by the Montreal Protocol. It has been recommended that eight chlorofluorohydrocarbons, the simplest of which is Freon-22 (CF_2HCl), be used as an alternative[42]. It is believed that Freon-22 is much less dangerous to the ozone layer than Freons such as $CFCl_3$ and CF_2Cl_2, because it reacts comparatively rapidly with OH radicals, i.e.

$$CF_2HCl + OH \rightarrow CF_2Cl + H_2O,$$

the rate constant being $k = 1.2 \times 10^{-12} \exp -(1100 \pm 150)/T \text{ cm}^3 \text{ s}^{-1}$, and penetrates the stratosphere to a much lesser extent. Thus through the interaction of the OH radicals with the alternative Freons, a tropospheric-stratospheric coupling is established between the chlorine family of anthropogenic origin and the ozone layer. Freons exert the principal destructive influence at a height of ~40 km where the rate of their photodissociation becomes appreciable.

The influence of heterogeneous tropospheric factors on the stratospheric ozone was estimated by the present authors together with Zvenigorodskii and Smyshlyaev. In particular, the following scenario was examined.

Suppose that the release of all the Freons is modelled by the release of Freon CF_2HCl in an amount of one million tonnes per year. In this case, a steady state would be established after approximately eighty years in which the O_3 content at a height of 38 km would diminish by 8% relative to the Freon-free atmosphere. By varying the rate constants for elution and the scattering of radiation by the cloud cover within reasonable limits and by postulating the heterogeneous destruction of OH and HO_2 radicals on the tropospheric background aerosol, it is easy to obtain a two–three-fold diminution of the concentration of tropospheric hydroxyls. This would lead in its turn to an additional decrease in the ozone concentration at a height of about 40 km by 10%, so that the overall fall in the content of O_3 at these heights would be by 18%. The total degradation of the ozone column after 80 years would be 3% under these conditions. Thus heterogeneous processes controlling the content of $\dot{O}H$ radicals determine also the ozone content in the upper stratosphere. The aerosol contaminants of the troposphere, leading to a decrease in its $\dot{O}H$ content and to an impairment of the purity of the troposphere, promote under these conditions the entry of the alternative Freons into the ozonosphere and an increase in the risk of the decomposition of the ozone layer.

The principal products of the oxidation of the majority of alternative Freons are compounds of the phosgene series[42]; in particular, in the case of CF_2HCl the product is CF_2O. The higher the concentration of tropospheric hydroxyls, the smaller the amount of Freons penetrating the stratosphere. However, vigorous oxidation of Freon occurs closer to the Earth's surface the lower the content of aerosols. The intensification of the reactions of $\dot{O}H$ with Freon leads to the accumulation of toxic compounds (phosgenes) in the lower part of the atmosphere. Thus by ejecting alternative Freons into the atmosphere, we can be faced by the extremely sad prospect of the replacement of the ozone problem by the phosgene problem. Such trade-off between the ecological and toxicological problems is merely a hypothetical variant. It may be that the decomposition of phosgenes in water drops, i.e.

$$CF_2O + (H_2O)_{ж} \rightarrow CO_2 + 2HF$$

will eliminate the toxicological risk of the alternative Freons. All this requires more complete quantitative tests.

4. Heterogeneous reactions in polar stratospheric clouds and Antarctic spring ozone holes

The sensational phenomenon of the sharp decrease in the concentration of ozone in the Antarctic during the spring, observed comparatively recently[43], has been adequately discussed in the scientific literature and in the publications for general consumption (see, for example, Karol'[20]). A central place has been assigned to this problem in the annual international reviews of the state of the ozone layer, including the latest collection.[44] We shall concentrate attention on the heterogeneous processes which are believed to occur in the establishment of the precritical spring situation and possibly also during the development of the ozone "hole". Without going into the details of the dynamics of the development and of the scale of the Antarctic ozone holes, we shall only emphasise that, according to the observations at the Halley Bay station (76° S, 27° W), the spring decrease in the ozone content in the Antarctic during the period from 1957 to 1985[43] did not begin until 1979. From 1979 until 1985, the overall ozone content in October fell from 300 to 200 Dobson units (1000 Dobson units correspond to a 1 cm thickness of the ozone layer at atmospheric pressure). Evidently the primary cause of this phenomenon is the anthropogenic release of Freons.[19]

It is believed at the present time that during the winter, when the stratosphere cools down and particles condense in polar stratospheric clouds (PSC), chemical processes leading to the removal of nitrogen oxides from the gas phase and the generation of molecules of the chlorine reservoir take place. These photochemically active chlorine components do not react during the winter with the PSC particles or with ozone in the gas phase or on the surface. During sunrise in the spring period, the reservoir chlorine molecules undergo photodissociation and are converted into a radical form which initiates the chain decomposition of ozone. This multistage concept is hardly complete in our view. We suggest that heterogeneous reactions can be also a direct and not merely an indirect cause of the decomposition of the Antarctic ozone. During the initial period of the polar night, after sunset there is a fairly rapid recombination of the active atmospheric components ($\dot{O}H$, ClO, and $\dot{H}O_2$) as well as the nitrogen oxides NO_x, which are converted into the reservoir gases H_2O, HCl, H_2O_5, HNO_3, H_2SO_4, and $ClONO_2$. The subsequent fate of the reservoir gases has been investigated in experiments under natural and laboratory conditions. In particular, it has been established that the coefficient of adhesion of the molecules of the acids HCl and HNO_3 to the surface of ice is close to unity[45,46] and that the composition of the PSC condensate is close to that of the nitric acid trihydrate[10] or contains 0.02–0.35 mol of HCl per mole of water[46] at temperatures below 195 K. Laboratory studies confirmed the conclusions reached from observations under

natural conditions that gas denitrification and dehydration reactions take place during winter (Scheme 1):

Scheme 1

(1) $N_2O_5 + (H_2O)_S \rightarrow 2(HNO_3)_S$,

(2) $N_2O_5 + (HCl/H_2O)_S \rightarrow (ClNO_2)_G + (HNO_3)_S$,

(3) $ClONO_2 + (H_2O)_S - (HOCl)_G + (HNO_3)_S$,

(4) $ClONO_2 + (HCl/H_2O)_S \rightarrow (Cl_2)_G + (HNO_3)_S$.

The subscripts G and S denote the gas and condensed phases respectively. In reactions (2)–(4) (Scheme 1), the chlorine component is converted into a new form, affording the readily photolysed reservoir gases Cl_2, HOCl, and $ClNO_2$ (or ClONO). They in fact ensure the development of the dramatic spring situation.

The values $\gamma_{O_3} \approx 10^{-6}$ attained under laboratory conditions in the study of the decomposition of ozone on ice and nitric acid particles[24] indicate the possibility, in principle, of the direct breakdown of O_3 during the long polar night.

Table 3. Heterophase reactions occuring under the conditions of the polar Antarctic night.

Reaction	Conditions	γ	Refs.
(1)	195 K	0.028±0.011	[47]
	185 K	$>10^{-3}$	[48]
(2)	$[HCl]/[H_2O] \leq 0.04$	~0.06	[47]
	—	$>3\cdot10^{-3}$	[48]
(3)	185–200 K	0.009	[49]
	—	0.02	[50]
	—	0.06	[45]
(4)	$[HCl]/[H_2O] = 0.015 \div 0.04$; 195 K	0.27	[45]
	$[HCl]/[H_2O] = 0.003 \div 0.01$; 200 K	$0.05 \div 0.1$	[50]

Measurements[24] are not inconsistent with estimates[47] according to which γ_{O_3}, γ_{NO}, and $\gamma_{NO_2} < 10^{-4}$ for ice. The results of studies on reactions (1)–(4) under conditions close to those during the Antarctic polar night (180–200 K) are presented in Table 3. It is seen that in all cases these low-temperature reactions proceed extremely effectively. Thus their characteristic time in polar stratospheric clouds does not exceed 24 h. The condensation of nitric acid has been reliably demonstrated in all four reactions. On the other hand, the gas-phase products and the possible routes to their further conversion have been less thoroughly investigated. In experiments[47,48] carried out using mass-spectrometric analysis, the products ClONO and $ClNO_2$ proved to be indistinguishable. Furthermore, one cannot rule out the possibility of their subsequent heterogeneous reactions.[45] It has been shown that HOCl is the gas-phase product of reaction (3). However, this is apparently merely an unstable intermediate, which reacts with ice, at least in the presence of $ClONO_2$, with formation of Cl_2O [50].

Although the measured rates of reaction (3) differ from one another by a factor of 6, they are nevertheless fairly high, so that this is not the reaction which limits the heterogeneous reaction of $ClONO_2$ in wintertime. The composition of products of reactions (2) and (3) (Scheme 1) and their behaviour in the presence of PSC require further refinement.

The heterogeneous reactions (1)–(4) in Scheme 1 lead to the capture of gas-phase nitrogen oxides and the formation of photochemically active gaseous Cl_2, HOCl, Cl_2O, and $ClNO_2$ molecules. It is at present difficult to say which of these makes the greatest contribution to the photolytic generation of Cl atoms at sunrise. However, the very fact of the high chlorine content in the radical form has been demonstrated by direct measurements of the concentration of ClO radicals[51,52,58], which at the beginning of the spring (September) at a height of about 20 km exceeds by a factor of 100 their concentration in the middle latitudes. Already in October, when the polar clouds break up and O_3 degradation processes cease, the Cl content in the Antarctic does not differ appreciably from its content in the middle latitudes. Apparently the main O_3 decomposition cycle is determined, as suggested by Molina and Milina[53] by the reactions

$$\begin{aligned} ClO + ClO + M &\rightarrow Cl_2O_2 + M \quad , \\ Cl_2O_2 + h\nu &\rightarrow Cl + ClO_2 \quad , \\ ClO_2 + M &\rightarrow Cl + O_2 + M \quad , \\ 2(Cl + O_3) &\rightarrow 2(ClO + O_2) \quad , \\ \hline 2O_3 + h\nu &\rightarrow 3O_2 \quad . \end{aligned}$$

The first, termolecular reaction which has been invetigated[54,55] limits the decomposition of O_3. Knowing the concentration ClO and the rate constant for this reaction, it is possible to calculate the rate of degradation of ozone, which proves to be close to the experimentally measured value. If the formation of Cl_2O_2 is indeed the rate-determining stage of the spring decomposition of O_3, then, by virtue of its non-linearity in relation to the chlorine content, its rate should change sharply with increase in the amount of Freons released into the atmosphere. This picture has in fact been observed since 1979 [43]. The recombination of ClO radicals can become dominant only in the presence of a low NO_2 content, but the rate of their reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$ is low. During the winter, the reservoir nitrogen oxide gases are converted into condensed nitric acid as a result of the occurrence of the heterogeneous reactions (1)–(4) (Scheme 1). Nitrogen oxides can therefore appear only after the evaporation of the PSC, which begins in October. The low NO_2 content in the winter and spring Antarctic atmospheres has been confirmed by many observations[55]. Apart from the purely chlorine-based zone decomposition cycle, a further two synergistic cycles with participation of BrO [56] or OH and HO_2 [57] radicals have been proposed. In the synergistic cycle

$$\begin{aligned} ClO + BrO &\rightarrow Cl + Br + O_2 \quad , \\ Cl + O_3 &\rightarrow ClO + O_2 \quad , \\ Br + O_3 &\rightarrow BrO + O_2 \quad , \\ \hline 2O_3 &\rightarrow 3O_2 \quad , \end{aligned}$$

note more than 10% of ozone relative to the purely chlorine-based cycle can decompose, since the BrO concentration is low compared

with that of ClO.[58] The hydrogen chloride cycle[57]

$$\begin{aligned} HOCl + h\nu &\rightarrow OH + Cl \quad , \\ Cl + O_3 &\rightarrow ClO + O_2 \quad , \\ OH + O_3 &\rightarrow HO_2 + O_2 \quad , \\ ClO + HO_2 &\rightarrow HOCl + O_2 \quad , \\ \hline 2O_3 &\xrightarrow{h\nu} 3O_2 \quad , \end{aligned}$$

is apparently relatively ineffective owing to the high probability of the destruction of OH radicals on the ice particles.[32] Thus the chlorine-based O_3 decomposition cycle with participation of the Cl_2O_2 dimer is apparently most effective.

After this review had been written, one of the authors received the manuscripts of papers[58,59] prepared for publication, which were sent by Prof. Brune. Brune and co-workers[59] carried out a detailed analysis of the contributions of various Antarctic ozone decomposition cycles on the basis of simultaneous measurements of the absolute concentrations of ClO, BrO, and O_3 carried out with an aeroplane in 1987 [58]. The latest data for the rate constants for the rate-limiting stages of the above homogeneous cycles (the ClO + ClO + M and ClO + BrO reactions[60]) and measurements under natural conditions[58] permitted the conclusion that the main contribution to the spring decomposition of ozone comes from the chlorine cycle and the chlorine-bromine cross cycle. In order to refine the contribution of the hydrogen chloride cycle, it is necessary to have direct measurements of the concentration of OH (or HO_2). According to estimates,[53] it is not more than 4%. The contribution of the first two cycles to the observed rate of the spring decomposition of O_3 can reach 40 and 20% respectively. In order to abolish the underestimate in the calculated rate, yet another catalytic cycle has been proposed:[59]

$$\begin{aligned} &ClO + O_3 + M \rightarrow ClO.O_3 + M (k = 2 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1} \text{ at 200 K}), \\ &ClO \cdot O_3 + h\nu \rightarrow ClO_2 + O_2 \quad , \\ &ClO_2 + M \rightarrow Cl + O_2 + M \quad , \\ &Cl + O_3 \rightarrow ClO + O_2 \quad , \\ \hline &2O_3 + h\nu \rightarrow 3O_2 \quad . \end{aligned}$$

Having included in the consideration also this sequence of reactions with the rate constant for the formation of complex $ClO.O_3$ indicated, it is possible to reconcile completely the experimentally observed kinetic relations for the spring decomposition of O_3 with the diurnal concentration of the ClO and BrO radicals. However, we believe that there is no need to introduce into consideration an exotic species such as the complex $ClO.O_3$. In order to account for the underestimate of the rate of the spring decomposition of ozone, one can examine the additional heterogeneous-homogeneous photolytic cycle

$$\begin{aligned} &ClO + PSC \rightarrow \tfrac{1}{2}(Cl_2 + O_2), \\ &Cl_2 + h\nu \rightarrow 2Cl \quad , \\ &2(Cl + O_3) \rightarrow 2(ClO + O_2) \quad , \\ \hline &2O_3 + PSC + h\nu \rightarrow 3O_2. \end{aligned}$$

The possibility of the existence of this hypothetical cycle has been confirmed by preliminary measurements of the probability of the destruction of ClO on the surface of ice ($\gamma_{ClO} \simeq 10^{-2}$).[47] A simple estimate showed that, when [ClO] = 2×10^9 cm^{-3}, the rate of decomposition of O_3 in the heterogeneous cycle can be close to the rate of its degradation in the homogeneous chlorine cycle. More detailed studies on the heterogeneous interaction of ClO radicals with the surface of ice are apparently necessary.

Yet another important heterogeneous reaction in the Antarctic spring may prove to be the process

$$ClO + (O_3)_{ads} \rightarrow OClO + O_2,$$

where $(O_3)_{ads}$ is the ozone molecule adsorbed on the PSC surface. This reaction can account for the variation of the ClO concentration over a period of 24 h. It is known that during the night ClO is almost fully converted into OClO. However, this does not lead to a change in $[O_3]$ because ozone molecules are regenerated during the day by the reactions:

$$\begin{aligned} &OClO + h\nu \rightarrow O + ClO, \\ &O + O_2 + M \rightarrow O_3 + M. \end{aligned}$$

The heterogeneous catalytic reactions

$$ClO + (H_2O)_s \rightarrow \tfrac{1}{2}(Cl_2 + O_2) + (H_2O)_s,$$

and

$$ClO + (O_3).(H_2O)_s \rightarrow OClO + O_2 + (H_2O)_s,$$

proposed here can undoubtedly play a definite part in the chemical reactions occurring in the spring in the Antarctic. As regards the winter preparatory period, here too the heterogeneous reactions of the ClO precursor gases (HOCl, Cl_2O, $ClNO_2$, and ClONO) with solid PSC particles can be important. Apart from the study of these heterogeneous reactions, it is also essential to carry out measurements of the HOCl, Cl_2O, $ClNO_2$, and ClONO concentrations under natural conditions. We should like to point out also the possible influence of the direct decomposition of O_3 on PSC particles on the dynamics of the formation of the ozone hole in the Antarctic spring. A model of this process includes the change in the vertical air circulation in springtime, when the warm air of the troposphere, depleted in ozone, rises to the stratosphere, diminishing thereby the ozone concentration in the lower stratosphere. Measurements[24] indicate the possible decomposition of O_3 (within the limits of 10%) on PSC particles during the long polar night. This can afford additional support to the dynamic model, because during the winter the circulation of air is directed downwards and one cannot rule out the possibility that towards spring the troposphere is more depleted in ozone than in the absence of the direct decomposition of stratospheric ozone.

5. The influence of volcanic eruptions on the ozone content of the stratosphere

Powerful volcanic eruptions, which include a series of eruptions of the Mexcian El Chichon volcano (17° N latitute) at the beginning of April 1982 have exerted a large-scale influence on the stratosphere. Thus the aerosol cloud formed after the eruption of El Chichon extended from the equator to 50° N latitude, whilst the duration of its development and relaxation exceeded one year (Fig. 3). The scale of the eruption can be imagined from the amount of SO_2 ejected (3.3 million tonnes). The photochemistry of the stratosphere can be influenced greatly also by the ejection of HCl and water vapour. The components of the ejected material are apparently initially concentrated at a height of 25–35 km. However, after a time, as a result of photochemical oxidation mainly in the Junge layer, sulphuric acid aerosols containing 75% H_2SO_4 and 25% H_2O accumulate. Fig. 3 shows a distinct negative correlation between the content of the aerosol component and the amount of ozone, which has been the subject of controversy since the instant of its

observation during the winter of 1982–1983. Without being able to consider at length problems of the formation of volcanic clouds and the modelling of the effects of a volcanic eruption on the thermal and radiation conditions in the stratosphere, we shall merely point out that, according to estimates[21,61,62], the observed decrease in the concentration of ozone cannot be accounted solely by the change in temperature and in the solar radiation fluxes. The O_3 content begins to decrease not sooner than half a year after the eruption and is correlated with the formation of secondary sulphuric aerosols in the Junge layer.

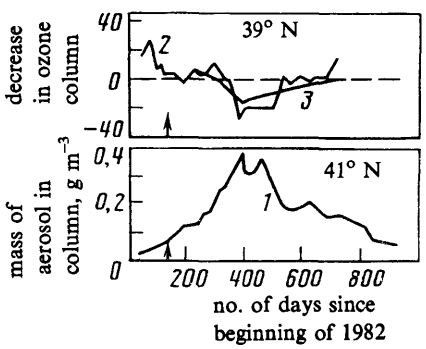


Figure 3. Variation of the contents of aerosols and ozone in the course of the evolution of the eruption cloud; *1*, aerosol; *2*, observed decrease in the amount of ozone of Dobson units (according to the data of Tolbert et al.[63]); *3*, calculated decrease in the amount of ozone for $\gamma_{OH} = 1$ (according to Anderson et al.[59]); the instant of the eruption of the El Chichon volcano is indicated by an arrow.

Two alternative models explaining the decrease in the amount of O_3 by the occurrence of heterogeneous reactions have been put forward recently. According to the first hypothesis[8,61,62], the decrease in the O_3 content in the cloud is caused by the heterogeneous destruction of OH radicals on the aerosol particles. The decrease in [OH] leads to an increase in [NO] and in the contribution of the nitrogen cycle (see above). The results of numerical modelling[59], based on the value $\gamma_{OH} = 1$, adopted on the basis of the measurements of γ_{OH} for ice and sulphuric acid[32] are presented in Fig. 3. Evidently the proposed hypothesis makes it possible to describe quantitatively the sharp diminution in the concentration of ozone in the volcanic cloud.

The second hypothesis is based on the measurements of the probabilities of the capture of HCl, $ClONO_2$ [63] and N_2O_5 [64] by the sulphuric acid solution and the temperature of the stratospheric volcanic clouds in wintertime (−65 °C). It follows from Table 4 that N_2O_5 is captured particularly effectively. On the hypothesis that nitric acid, evolved into the gas phase, is the product of the reaction of N_2O_5 with the H_2SO_4/H_2O surface and that the heterogeneous interaction of HCl and $ClONO_2$ leads to the generation of active chlorine, it has been possible to demonstrate[21] a decrease in the O_3 content in volcanic clouds after the eruption of the El Chichon volcano. Aerosols apparently exert an extremely varied influence. On the one hand, they convert N_2O_5 and nitrogen oxide into nitric acid, reducing the strength of the nitrogen-based O_3 decomposition cycle. On the other hand, their reactions with HCl and $ClONO_2$ generate chlorine, which initiates the operation of the chlorine-based ozone decomposition cycle:

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \quad , \\ \underline{O + ClO \rightarrow Cl + O_2 \quad ,} \\ O + O_3 \rightarrow 2O_2 \quad . \end{array}$$

Under the usual conditions, the effectiveness of this cycle in the lower stratosphere is low.

Table 4. Probabilities of the capture of HCl, N_2O_5, and $ClONO_2$ by the sulphuric acid surface at −65 °C.

γ	H_2SO_4, %			Refs.
	65	70	75	
γ_{HCl}	$1.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	[63]
γ_{ClONO_2}	—	$2.5 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	[63]
$\gamma_{N_2O_5}$	—	—	0.06	[64]

The second model of the heterogeneous decomposition of ozone in volcanic clouds is significantly more complex than the first, associated with the heterogeneous destruction of OH radicals. It contains more non-monitored parameters.

IV. Chemical processes in cloud drops

1. General characteristics of the aqueous component of the troposphere

In the set of objects and phenomena in the heterogeneous chemistry of the atmosphere, the chemistry of the processes in the liquid drop phase—in clouds, rain drops, mists, and smoke—is an important component which has been studied inadequately. Certain physical and physicochemical characteristics of these heterogeneous components of the troposphere are listed in Table 5.

On average, 54% of the Earth's firmanent is covered by clouds,[68] the thickness of the cloud layer amounting to tens and thousands of metres. Thus an appreciable proportion of the troposphere is constantly filled with clouds having a high moisture content. The air also moves constantly through the cloud layer at a velocity ranging from 0.1 to 10 m s^{-1} [69]. This flow of gases leads to a constant renewal of the gaseous environment of the cloud drops and hence to a virtual constancy of the gas composition outside and within the cloud layer. For these reasons, attention will be concentrated below on the cloud drops and the rain drops "associated" with them. The characteristic lifetime of the drops (from minutes for rain drops to a period of the order of 1 h for cloud drops) should be included among their main properties[70].

The dynamics of the formation and growth of cloud drops has been examined from different standpoints, with and without allowance for the dissolution in the drops of gaseous substances,

with variation of the size distribution for the condensation centres-nuclei, etc. These questions have been discussed fairly widely by Hill[71] and in the Proceedings of the Leningrad Conference on "Models of the Contamination of the Atmosphere and Their Employment" (1986). In the first seconds of drop formation, their size distribution ranging from 1 to 5 μm is characterised by a descending curve. In the 300th second of the life of the drops, a fairly narrow size distribution is attained with the most probable diameter $d \simeq 8$ μm. The average size of the cloud drops listed in Table 5 is a result of the averaging of the size distribution during the lifetime of the drop, which varies as a function of time.

Table 5. Physicochemical characteristics of the liquid drop constituents of atmospheric moisture.

Medium	Drop radius, μm	Moisture content, g m^{-3}	pH	Ionic strength	Refs.
Smoke	0.3—3	10^{-5}—10^{-4}	1—8	1	[65]
Mist	10	0.02—0.2	2—6	10^{-3}—10^{-2}	[66]
Cloud	10	0.1—3	3—6	10^{-3}—10^{-2}	[67]
Rain	200—2000	0.1—1	4—5	10^{-4}	[67]

An interesting effect of the growth of the drops with increase in their sulphuric acid content, first observed by Foster[72], has been thoroughly analysed[73]. On the whole, the physical picture of the formation and evolution of cloud drops has been studied in greater detail than the chemical processes in them.

Under natural conditions, chemical reactions take place in an open heterogeneous gas—liquid system; on the other hand, in the majority of laboratory studies, the reaction is investigated in solutions in the absence of transfer of substances from one phase to another.

The chemical process in cloud drops is accompanied by a change in the pH of the medium by 1—3 units and the corresponding change in the concentrations of the substances (including catalysts) in the ionised form; on the other hand, under laboratory conditions, one endeavours to discover the dependence of the rate of reactions on a particular parameter while keeping the remaining parameters constant.

The characteristic concentrations of stable substances in cloud drops (10^{-10}—10^{-5} M) are much lower than in the usual laboratory studies (10^{-4}—10^{-2} M). For such a large difference between the concentrations parameters, the extrapolation of the kinetic relations to the region of low concentrations is riddled with errors whose scale is difficult or impossible to estimate.

2. Kinetic analysis of processes leading to the formation of sulphate ions in cloud drops

The origin of the chemistry of clouds can be traced back to 1852 when Smith detected sulphate ions in the rain water of Manchester[74]. Subsequently ammonium ions and nitric acid were found in rain[75]. These are in fact the three main components of rain water whose concentration reaches 10^{-3} M for NH_4^+ and SO_4^{2-} and 10^{-4} M for NO_3^- in acid rain drops.

As industry developed and the analytical methods became more sensitive in the twentieth century, increasingly concentrations of the iron, manganese, lead, arsenic, mercury, etc. impurities began to be detected in rain deposits and in the snow cover. However, chemico-atmospheric studies during the last decade have shown that most of these substances are absent from cloud drops and are entrained by rain drops or are deposited on the snow cover from the layers of the troposphere near the earth. On the other hand, direct measurements have established the presence in cloud drops of iron (10^{-7}—10^{-4}) and manganese (10^{-8}—10^{-5} M) ions[76]. The anthropogenic origin of these ions is indicated by the approximately fivefold difference beween the contents of transition metal (predominantly iron) compounds in air over cities and over regions remote from cities. Hydrogen peroxide[77,78], formaldehyde, formic acid[79], methanesulphonic acid[80], and other substances have been detected in rain and cloud drops at variable concentrations, their amount being usually an order of magnitude smaller than that of sulphate, ammonium, and nitrate ions.

Analysis of the composition of rain drops does not require special aerological equipment. However, rain drop data are not particularly suitable as a quantitative characteristic of the composition of cloud drops. Despite the short time of their flight through the lower layers of the troposphere, they succeed in absorbing various gaseous substances and dust particles. Other processes also take place, as a result of which rain drops and cloud drops differ not only in composition but also in other fundamental properties (Table 5). The concentration of basic components in rain drops is usually lower than in cloud drops, although the opposite instances are also encountered. However, at a qualitative level, one can infer the "basic" chemical composition of cloud drops from the composition of the rain water.

Aerochemical studies have played and continue to play an important role in the understanding of the liquid-phase processes in the troposphere. Unfortunately, the present authors are unaware of any aerochemical study in which the dynamics of the increase in the NH_4^+, SO_4^{2-}, and H^+ concentrations in the drops of the cloud layer was traced and which was supplemented by measurements of the local gas-phase SO_2, H_2SO_4, HNO_3, NH_3, O_3, and H_2O_2 concentrations in this layer. Without these data, the question of the role of cloud drops—*concentrators* of the water-soluble oxidation products formed in the gas phase or *reactors* in which oxidation processes occur at a rate which is greater than, comparable to, or lower than in the gas phase—cannot be resolved with complete certainty. One should add that such measurements are by themselves not informative because the cloud is not an assembly of drops of "equal age"—drops are being constantly formed in the cloud. Formal kinetic analysis of the processes occurring in cloud drops is thus all the more important. The aim of such analysis is to establish the relations governing the formation of the oxidation products using the results of studies on oxidation processes in solutions. At the level of the mechanism of elementary reactions in the absence of adequate information about the rate constants, this problem reduces to determining the numerical rate constants for which oxidation products may be formed at the concentrations corresponding to the aerochemical data. An independent but important aspect of tropospheric calculations is comparison of the rates of the gas-phase and liquid-phase reactions involving the loss of free radicals, in the first place OH and HO_2. In particular, information about the Henry constants for substances A, i.e. $K_H = [A]/p_A$ mol litre^{-1} atm^{-1} (Table 6), is essential for the solution of such problems.

At pH $\leqslant$ 6 typical for cloud drops, the real solubility is characterised by the K_H of only the substances which do not enter into further reversible, chemical interactions with water. Among the substances listed in Table 6, this applies to only NO, CH_3OH, O_2, O_3, and H_2O_2. In order to calculate the equilibrium concentrations of other substances, it is necessary to take into account the proportions of the various forms in solution, so that the values of K_H characterise only the ratio $[A.H_2O]/p_A$. Thus the real solubility of CH_2O, which is in equilibrium with the free diol form $CH_2(OH)_2$, is reflected by the effective constant $K'_H = 6.3 \times 10^3$ mol litre atm^{-1}. Sulphur dioxide is present in solution in the forms $SO_2.H_2O$ (H_2SO_3), HSO_3^-, and SO_3^{2-} and the dissociation constants K_1, K_2, etc. have to be known in order to calculate the solubility. The characteristic time of attainment of acid-base equilibria of the substances in solutions is incomparably shorter than the rates of their possible chemical reactions.

Table 6. Henry constants (mol $litre^{-1}$ atm^{-1}) for various substances present in the troposphere at 298 K.

Substance	K_H	Substance	K_H
SO_2	1.23	CH_3OH	220
NH_3	58	CH_2O	2
NO	$2 \cdot 10^{-3}$	HCOOH	83
NO_2	$7 \cdot 10^{-3}$	O_2	$1.6 \cdot 10^{-3}$
HNO_2	50	O_3	$1.1 \cdot 10^{-2}$
HNO_3	$2 \cdot 10^5$	H_2O_2	$1.6 \cdot 10^5$

The problem of the characteristic time of attainment of the gas–liquid equilibrium is more complex, since its solution requires that account be taken of the molecular diffusion of substances from the surface into the bulk of the drop, of the gas flux, of the drop diameter, etc. Analysis carried out in relation to SO_2 [81–83] showed that, at pH $\leqslant$ 6 and at the characteristic tropospheric SO_2 concentrations, the time of attainment of the gas–liquid equilibrium is negligible (< 1 s) compared with the lifetime of the drop. Thus, in the analysis of the reactions of substances in drops, one can use the equilibrium values of $[HSO_3^-]$ as well as $[O_2]$ and $[O_3]$, since the solubilities of the latter substances are low and the O_2 and O_3 fluxes are intense. Turning to substances with a high solubility (H_2SO_4, HNO_3, H_2O_2, NH_3), it is essential to estimate quantitatively their transfer to the drops at the specified concentrations of the substances in the gas and for the specified drop diameters. The equilibrium concentrations of the substances in the drops at different temperatures and at different concentrations of the substances in the gas phase are calculated from the equations[84]:

$$[SO_2]_0 = p_{SO_2}(1.23 \exp\{3120\, t\})\{1 + (1.7 \cdot 10^{-2} \exp 2090t)/[H^+]\},$$

$$[NH_3]_0 = p_{NH_3}(58 \exp\{4035\, t\})\{1 + 1.7 \cdot 10^{-5} \exp(-4325t)/[OH^-]\},$$

$$[O_3]_0 = p_{O_3} \times 1.1 \times 10^{-2} \exp\{2500t\},$$

$$[H_2O_2]_0 = p_{H_2O_2} \times 1.6 \times 10^5 \exp\{6600t\}, \text{ etc.}$$

where $t = 1/T - 1/298$.

At heights of 1–5 km, the temperature differs from the terrestrial temperature by 6–30 K. At an average height of 1.5 km, which is close to the height of the maximum moisture content, the solubilities of the gases in the drops are assumed equal to the solubilities at 280 K. The concentrations of the test substances in the gas phase corresponding to this height[85] are listed in Table 7.

Table 7. Characteristic concentrations of SO_2 and of its potential oxidants in the background atmosphere at a height of 1.5 km at 280 K [85].

Substance X	$[X]_G$, cm^{-3}	p, atm	$[X]_{soln}$, M
SO_2	$3 \cdot 10^9$ (Ref.86)	$1.1 \cdot 10^{-10}$	$7.8 \cdot 10^{-12}/[H^+]$
O_2	$4 \cdot 10^{18}$	0.15	$2.7 \cdot 10^{-4}$
O_3	$7 \cdot 10^{11}$	$2.6 \cdot 10^{-8}$	$5.2 \cdot 10^{-10}$
H_2O_2	$1.1 \cdot 10^{10}$	$4 \cdot 10^{-10}$	$3 \cdot 10^{-4}$

The quoted concentration of H_2O_2 in solution is a maximum, since all the concentrations of the substances belonging to the odd hydrogen family were calculated on the assumption of a high intensity of illumination and a high humidity[85]. Under the conditions of the real background atmosphere, the H_2O_2, HO_2, and OH concentrations can be several times smaller. Taking into account this correction, one can assume that the value of $[H_2O_2]_{soln}$ agrees with the experimental concentration of hydrogen peroxide in the rain drops[78,79].

The problem of the nature of the drops at pH→3, which fall in the form of acid rain and have negative ecological consequences for soil and water catchment areas, is important in the chemistry of the cloud layer. Clouds consisting of such drops are formed in the presence of an SO_2 content many times greater than its content in the background atmosphere.

We are unaware of attempts at a chemical interpretation of the mechanism of the formation of acid cloud drops. As regards the background atmosphere, the potential possibility of the occurrence in the latter of processes involving the oxidation of sulphite ions by oxygen, ozone, and hydrogen peroxide and of the catalytic acceleration of the oxidation of sulphide ions under the influence of iron and manganese ions has been considered.

During the lifetime of a cloud drop in the background atmosphere ($\sim 10^3$ s), approximately 10^{-4} M sulphate ions accumulate together with a comparable amount of ammonium ions and the characteristic pH is 4.5–4.7.[87] At pH 3–6, the dominant form in which SO_2 is present in solution is HSO_3^-, since $K_1 = 1.7 \times 10^{-2}$ and $K_2 = 6 \times 10^{-8}$ M.

$$[SO_2]_0 = p_{SO_2} K_H \{1 + K_1/[H^+] + K_1K_2/[H^+]^2\}\, M.$$

The maximum HSO_3^- concentration at pH 6 is 8×10^{-6} M; as sulphate is formed and the acidity increases to pH 4.7, the maximum HSO_3^- concentration diminishes by a factor of approximately 20. The transition from HSO_3^- to SO_4^{2-} as $\overline{[HSO_3^-]} \simeq 2 \times 10^{-6}$ M takes place at an average rate $\overline{W} \simeq 10^{-4}/10^{-3} = 10^{-7}$ mol $litre^{-1}$ s^{-1}.

We shall compare the above value of $\overline{W}$ with the available rates of oxidation of sulphite ions by oxygen, ozone, and hydrogen peroxide. Their oxidation by oxygen and ozone and an analysis of all the previous studies has been carried out in greatest detail by Larson et al.[87] In the pH range 4–12, the rate of oxidation is described by the expression

$$\frac{d[SO_4^{2-}]}{dt} = \{4.8\cdot10^{-3} + 8.9[H^+]^{0.5} + 3.9\cdot10^{-12}[H^+]^{-1}p_{O_2}\}\cdot\frac{6\cdot10^{-8}[HSO_3^-]}{[H^+]}$$

for O_2 and by

$$\frac{d[SO_4^{2-}]}{dt} = 4.4\times10^4[O_3][HSO_3^-][H^+]^{0.1} \text{ mol litre}^{-1}\text{ s}^{-1}.$$

for the oxidation by ozone.

At concentrations characteristic of cloud drops, these rates are of the order of 10^{-9} and 10^{-11} mol litre^{-1} s^{-1} respectively.

The catalytic oxidation of sulphite in the presence of iron ions at the real HSO_3^- and Fe^{3+} concentrations in the pH range 4–12 was investigated using radiochemical monitoring[88]. At pH 4.9, we have

$$-\frac{d[HSO_3^-]}{dt} = 10^2[Fe^{3+}]_0[HSO_3^-] \text{ mol litre}^{-1}\text{ s}^{-1}.$$

According to the data of Brimblecome and Spedding[88], the pH dependence of the rate constant has a maximum at pH 6. Using the maximum value ($\sim2.5\times10^2$) and the HSO_3^- concentration corresponding to pH 6, it is possible to estimate the minimum concentration of iron ions at which $\overline{W} = 10^{-7}$ mol litre^{-1} s^{-1} as 5×10^{-5} M. This value lies in the range of the limiting concentrations of Fe^{3+} in cloud drops[76], which, however, corresponds not to the background atmosphere but to a highly polluted atmosphere.

Unfortunately such accurate studies on the catalysis of oxidation by manganese ions at concentrations close to those obtained in nature have not been found in the literature. It has been noted that Mn^{2+} ions are more effective as a catalyst of the oxidation of sulphite ions than iron ions[89]. On the other hand, quantitative studies have been carried out in the ranges of $[Mn^{2+}]$ and $[HSO_3^-]$ which differ from the real concentration ranges. Thus the following expression has been put forward[90]:

$$-\frac{d[HSO_3^-]}{dt} = 16[Mn^{2+}]^2.$$

It was obtained for $[Mn^{2+}] = (0.2-5)\times10^{-3}$ M and $[HSO_3^-] = 10^{-3}$ M.

In a later study[91] the equation

$$W = 4.7[H^+][Mn^{2+}]^2,$$

was proposed for the ranges pH 0–3, $[Mn^{2+}] = 10^{-5}-10^{-3}$ M, and $[HSO_3^-] = 10^{-4}-10^{-3}$ M. The equation

$$W = 25[H^+][Mn^{2+}][HSO_3^-],$$

was put forward for the same pH range and $[Mn^{2+}]$ and $[HSO_3^-] \leqslant 10^{-6}$ M.

When this relation is extrapolated to pH 6, it is found that, in order to attain $W = 10^{-7}$, it is sufficient to have a concentration $[Mn^{2+}] \simeq 10^{-9}$ M.

However, in the presence of ferric ions the effective rate constant, which in the given instance is $25[H^+]^{-1}$, by no means varies linearly with $[H^+]^{-1}$ in the region with pH > 4 (this is apparently associated with the hydrolysis of metal ions). Whatever the true state of affairs, before catalysis by Mn^{2+} ions is subjected to a study similar to that carried out for ferric ions[88] the problem of the possible accumulation of sulphates in drops of the background atmosphere as a result of the catalytic oxidation of sulphite in the presence of manganese ions will remain open.

The interaction of sulphite ions with H_2O_2 constitutes the basis of the analytical method for the determination of SO_2, H_2SO_3, and HSO_3^-. The process is autocatalytic. The dependence of the rate of reaction on the reactant concentrations in the pH range 4–8 assumes the following form according to Hoffman and Edwards[92]:

$$-\frac{d[SO_2]_0}{dt} = [H_2O_2][SO_2]_0\{[H^+]/[H^+] + 6\cdot10^{-8}\}(5.8\cdot10^7[H^+] + 7.2\cdot10^2[HA])^{\ddagger}$$

At pH 6 and the corresponding H_2O_2 and HSO_3^- concentrations (see Table 7), the rate of reaction $W = 1.3\times10^{-7}$ mol litre^{-1} s^{-1}, which agrees with the value of $\overline{W}$.

The process considered differs from all those examined previously by the fact that its rate under the conditions of cloud drops does not diminish with decrease in the HSO_3^- concentration, since the fall in the equilibrium value of $[HSO_3^-]$ induces an increase in $[H^+]$ in strict agreement[92] with the stoichiometry of the reaction

$$2HSO_3^- + H_2O_2 \rightarrow + 2SO_4^{2-} + 2H^+.$$

The approximate kinetic analysis carried out leads to the conclusion that the most probable oxidation process in the cloud drops of the background atmosphere is the interaction of HSO_3^- with H_2O_2. In recent years, a similar view has been expressed frequently in a qualitative form, but attention has not been turned to the catalytic nature of this reaction. In mathematical models (see, for example, Hill et al.[93]), the rate of formation of sulphate ions was described by the equation

$$\frac{d[SO_4^{2-}]}{dt} = k_{H_2O_2}[H_2O_2][HSO_3^-] + k_{O_3}[O_3][HSO_3^-],$$

i.e. without taking into account the role of hydrogen ions as the catalyst. Nor can one rule out the possibility of the catalytic oxidation of HSO_3^- with participation of Mn^{2+} ions, although the characteristics of this process at the concentrations attained in cloud drops are not available.

3. Gas–liquid models of the formation of acid drops in the background and contaminated atmospheres

In a contaminated atmosphere, the average rate of oxidation of sulphite ions should be ten and more times higher than in the background atmosphere in order to ensure the formation of 10^{-3} M SO_4^{2-} after approximately 10^3 s. At first sight, the formation of sulphate can be explained by the autocatalytic oxidation of sulphite by hydrogen peroxide, by substituting in the corresponding equation the values of p_{SO_2} which exceed by a factor of 10 or more the values

‡ A misprint occurred in the communication of Hoffman and Edwards[92]: instead of 5.8×10^7, 5.8×10^1 is printed in the text. It is easy to demonstrate that the latter figure is erroneous by carrying out an approximate calculation of the characteristic reaction time at pH 4.5, which, was stated by the authors[92] becomes less than 2.5 ms and measurements by the stopped flow method become impossible.

of p_{SO_2} in the background atmosphere. However, in a contaminated atmosphere not only p_{SO_2} but also p_{CO} is higher than in the background atmosphere. On the other hand, the reaction of CO with OH constitutes one of the most important pathways leading to the loss of OH. An increase in p_{CO} entails a decrease in the stationary OH, HO_2, and H_2O_2 concentrations. On the other hand, when the H_2O_2 concentration diminishes by an order of magnitude, the possibility of such explanation evidently disappears. Attention should be drawn also to the fact that the bulk of sulphate ions (from 10^{-4} to 10^{-3} M) should be formed in the pH range from 4 to 3, i.e. for $[HSO_3^-]_0$ lower by a factor of 10 than in the background atmosphere. All these factors preclude the justification of a chemical mechanism of the formation of drops in acid clouds on the basis of the reactions considered. One cannot rule out in any way the possibility that in this case a physical mechanism of the absorption of H_2SO_4 by drops, and not a chemical mechanism, acquires decisive importance. The distribution of H_2SO_4 and HNO_3 between the gas and liquid phases is displaced towards the latter so much that at their typical concentrations in acid drops (10^{-3} and 10^{-4} M) and in the gas (10^{-11} and 10^{-10} atm [86]) the acid concentration can be regarded as equal to the product of the lifetime of the drops and the flux of the acid from the gas to the drops. For $[H_2SO_4]_G \simeq 2 \times 10^8$ cm^{-3} and for a drop diameter of 10 μm, the total H_2SO_4 flux is $\sim 10^5$ mol^{-1} s^{-1}.

Thus for an accommodation coefficient $\gamma \simeq 10^{-1}$, the accumulation of sulphate ions in drops can be explained by the absorption of H_2SO_4 from the gas phase.

Assuming that $\gamma \simeq 10^{-2}$ for H_2SO_4, as is usually done in the literature in the absence of measured values, we shall consider all the possibilities of the chemical route to the accumulation of sulphuric acid. The most important factor is that the flux of HO_2 and OH from the gas to the drops can significantly exceed the rate of formation of these radicals in the drops as a result of the photolysis of O_3 and H_2O_2 if the values of γ for the radicals are assumed to be 10^{-2} [94–96].

The first chemical-mathematical model of the oxidation processes in the drops of sea clouds taking into account the OH and HO_2 fluxes[97] included the following reactions (Scheme 2);

Scheme 2

(1) $\dot{O}H + HSO_3^- \rightarrow \ldots \rightarrow SO_4^{2-} + 2H^+$,
(2) $\dot{O}H + HSO_3^- \rightarrow H_2O + \dot{SO}_4^-$,
(3) $OH + CH_2(OH)_2 \rightarrow HCOOH + \dot{H}O_2$,
(4) $\dot{O}H + HCOOH \rightarrow CO_2 + H_2O + \dot{H}O_2$,
(5) $OH + H_2O_2 \rightarrow H_2O + HO_2$ and the equilibria $H\dot{O}_2 \rightleftarrows H^+ + \dot{O}_2^-$ and $\dot{C}l + Cl^- \rightleftarrows \dot{Cl}_2^-$,
(6) $\dot{H}O_2 + O_3 \rightarrow 2O_2 + \dot{O}H$,
(7) $S\dot{O}_4^- + Cl^- \rightarrow SO_4^{2-} + \dot{C}l$,
(8) $\dot{C}l + \dot{O}_2^- \rightarrow Cl^- + O_2$,
(9) $\dot{H}O_2 + \dot{O}_2^- \rightarrow HO_2^- + O_2$.

On the assumption that $\gamma \simeq 10^{-2}$, the $H\dot{O}_2$ and $\dot{O}H$ fluxes were assumed to be 9×10^{-9} and 1.4×10^{-9} mol litre^{-1} s^{-1} respectively, while $[H_2O_2] = 5 \times 10^{-5}$ M.

Within the framework of this model it proved possible to obtain the value $[SO_4^{2-}] = 8 \times 10^{-6}$ M, which is close to the value characteristic of sea clouds. The study quoted above[97] is particularly important also, because the rate constants for the elementary radical reactions were used in it for the first time in considering the oxidation processes in cloud drops. The reason why the ratio of the $H\dot{O}_2$ and $\dot{O}H$ fluxes in the above studies[97] is approximately 7 whereas in the tropospheric zone $[H\dot{O}_2]_G/[\dot{O}H]_G > 10^2$ and the molecular-kinetic characteristics of $H\dot{O}_2$ and $\dot{O}H$ do not differ all that much remains obscure.

In subsequent years it proved possible to determine experimentally the accommodation coefficients of all three tropospheric substances. These values are 0.11 for SO_2 [98], 0.18 for H_2O_2 [98], and 0.27 for $H\dot{O}_2$ [36] The last figure is particularly important, because it increases the calculated $H\dot{O}_2$ flux into the drops by a factor of approximately 30. In this connection, we attempted the mathematical modelling of the sulphite oxidation process in cloud drops via a radical mechanism. It is noteworthy that the true mechanism of this process—one of the first examples of radical chain reactions in solutions[99]—has not been ultimately elucidated to this day[100]. It is the general view that microadmixtures of variable-valence metal ions participate in the initiation stage. The radical-chain mechanism put forward by Backstrom[101] can be represented in the form (Scheme 3)

Scheme 3

$$i \rightarrow H\dot{S}O_3 (SO_3^{\cdot-})$$
(1) $SO_3^- + O_2 \rightarrow SO_5^{\cdot-}$
(2) $SO_5^{\cdot-} + SO_3^{2-} \rightarrow SO_5^{2-} + SO_3^{\cdot-}$ } ν
(3) $SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-}$
(0) $SO_5^- + SO_3^{\cdot-} \rightarrow O_2 + S_2O_6^{2-}$.

The reaction is sensitive to copper ion microimpurities present in solution at concentration of the order of 10^{-12} M (in an alkaline medium)[101]. When carefully purified reagents and deionised triply distilled water are used, initiation is effective by iron ions at concentrations of the order of 10^{-8} M [88]. The unsatisfactory reproducibility of the experiments and the high sensitivity of the rates reactions to small amounts of added alcohols and other inhibitors indicate a considerable chain length. As kinetic data accumulate, indicating that at pH < 6 the rate of reaction is independent of p_{O_2} [87], the chain termination reaction has come to be represented in the form

$$SO_5^- + SO_5^- \rightarrow S_2O_6^{2-} + 2O_2.$$

The ideas about the chain propagation put forward by Hayon et al.[102] are based on the study of the reactions of sulphur–oxygen radical-ions ranging from SO_2^- to SO_5^-. The authors[102] concluded that, after the formation of the sulphate ion and the SO_4^- radical-ion, the chain propagation in reaction (2) takes place as a result of the following process:

$$SO_4^{\cdot-} + HSO_3^- \rightarrow SO_4^{2-} + H^+ + SO_3^-.$$

The legitimacy of including in the process mechanism of reactions involving SO_4^- has been confirmed by measurements of the rate constants for the reactions of SO_5^- and SO_4^- with alcohol[102]. The interaction of alcohol with SO_4^-, and not with SO_5^-, is more effective.

Comparison of the values of pK for H_2O and $H\dot{O}$ and also for H_2O_2 and $H\dot{O}_2$ makes it possible to assume with a high degree of probability that in the range 3 < pH < 6 the dominant species are SO_3^- (and not $H\dot{S}O_3$) and $H\dot{S}O_5$ (and not SO_5^-) ($K_2 \simeq 10^{-10}$ mol litre^{-1} for H_2SO_5). Taking into account all the considerations

described, the mechanism of the oxidation of HSO_3^- can be represented by Scheme 4:

Scheme 4

$$i \rightarrow SO_3^{\cdot-}$$

(1) $SO_3^{\cdot-} + O_2 \xrightarrow{H} H\dot{S}O_5$,

(2) $H\dot{S}O_5 + HSO_3^- \rightarrow 2H^+ + SO_4^{2-} + SO_4^{\cdot-}$,

(3) $SO_4^{\cdot-} + HSO_3^- \rightarrow SO_4^{2-} + H^+ + SO_3^{\cdot-}$,

(0) $H\dot{S}O_5 + H\dot{S}O_5 \rightarrow 2O_2 + 2H^+ + S_2O_6^{2-}$.

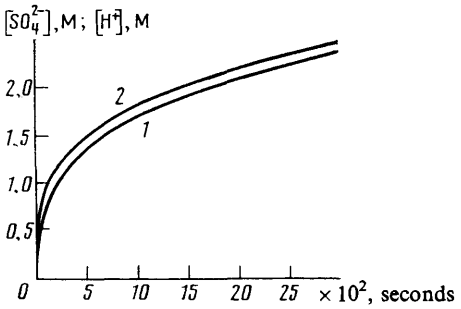


Figure 4. Kinetics of the accumulation of SO_4^{2-} (curve *1*) and H^+ (curve *2*) ions in water drops (calculated data).

We may note that the nature of the initiation reactions still remains obscure. This can be easily demonstrated by comparing the mechanism just presented or the one considered previously, without the participation of $SO_4^{\cdot-}$, with the experimental expression for the rate of reaction:

$$W = (k + k_2[H^+]^{0.5})[HSO_3^-],$$

which follows from studies analysed by Larson et al.[87] Taking into account the large chain length for the oxidation of sulphite, we obtain

$$W_i = k_0 W^2/k_2^2[HSO_3^-]^2 \quad \text{or} \quad W = [HSO_3^-]\, k_2^{0.5} \sqrt{W_i}/k_0^{0.5},$$

i.e. W_1 is independent of both $[O_2]$ and $[HSO_3^-]$. The question concerning the nature of initiation loses its importance in the presence of an external source of free radicals. In our model, as in the study of Chameides and Kiang,[97] the initiation reaction is that between HSO_3^- and the $\dot{O}H$ radicals entering the drops from the gas phase. Since the $H\dot{O}_2$ concentration and hence the flux of $H\dot{O}_2$ into the drop are approximately 10^2 higher than the flux of $\dot{O}H$, we included in the model the following chain termination reaction

$$H\dot{S}O_5 + H\dot{O}_2 \rightarrow HSO_5^- + H^+ + O_2,$$

as well as the reaction of HSO_3^- with H_2O_2 considered above. Apart from the $\dot{O}H$ and $H\dot{O}_2$ fluxes, account was also taken of the fluxes of H_2O_2 and NH_3 into the drop from the gas phase.

$\gamma \simeq 0.1$ was adopted for OH. The fluxes of H_2O_2 both into the drop and from the drop were taken into account. Analysis based on Smoluchowski's formula showed that an equilibrium distribution of H_2O_2 between the gas and liquid phases is established after 10 s (for drops with $d = 10$ μm). The NH_3 flux was regarded as a variable parameter normalised by the condition that in an acid drop $[NH_4^+]$ should be close to $[SO_4^{2-}]$. The values of $[H\dot{O}_2]_G$, $[\dot{O}H]_G$, and $[H_2O_2]_G$ were assumed to be 10 times smaller than in the background atmosphere. Thus the scheme includes the following fluxes of species from the gas into the drop:

$$OH \rightarrow 10^{-8}\ HO_2 \rightarrow 5 \times 10^{-7}\ NH_3 \rightarrow 10^{-5}\ H_2O_2 \rightarrow 10^{-5}\ \text{mol litre}^{-1}\ \text{s}^{-1},$$

and the following elementary reactions (Scheme 5)

Scheme 5

(1) $\dot{O}H + HSO_3^- \rightarrow H_2O + SO_3^{\cdot-}$, $k_1 = 9.5 \cdot 10^9$ litre mol^{-1} s^{-1} (Ref.103)

(2) $SO_3^{\cdot-} + O_2 \xrightarrow{H^+} H\dot{S}O_5$, $k_2 = 3 \cdot 10^9$ » (Ref.102)

(3) $H\dot{S}O_5 + HSO_3^- \rightarrow 2H^+ + SO_4^{2-} + SO_4^{\cdot-}$, $k_3 = 5 \cdot 10^9$ » —

(4) $SO_4^{\cdot-} + HSO_3^- \rightarrow SO_4^{2-} + H^+ + SO_3^{\cdot-}$, $k_4 = 1.5 \cdot 10^9$ » (Ref.102)

(5) $H\dot{S}O_5 + H\dot{S}O_5 \rightarrow 2H^+ + S_2O_6^{2-}$, $k_5 = 1.0 \cdot 10^7$ » (Ref.102)

(6) $H\dot{S}O_5 + H\dot{O}_2 \rightarrow O_2 + H^+ + HSO_5^-$, $k_6 = 10^8$ » —

(7) $\dot{O}H + H_2O_2 \rightarrow H_2O + H\dot{O}_2$, $k_7 = 4.5 \cdot 10^7$ » (Ref.103)

(8) $\dot{O}H + H\dot{O}_2 \rightarrow H_2O + O_2$, $k_8 = 7.0 \cdot 10^9$ » (Ref.103)

(9) $H\dot{O}_2 + H\dot{O}_2 \rightarrow H_2O_2 + O_2$, $k_9 = 8.1 \cdot 10^5$ » (Ref.103)

(10) $H\dot{O}_2 + O_2^{\cdot-} \rightarrow HO_2^- + O_2$, $k_{10} = 9.5 \cdot 10^7$ » (Ref.103)

(11) $H_2O_2 + H^+ + HSO_3^- \rightarrow H_2O + 2H^+ + SO_4^{2-}$, $k_{11} = 5.8 \cdot 10^7$ » (Ref.92)

Apart from the values of k_i and $pK_{HO_2} = 4.88$ known from the literature[104], the approximate values of k_3 and k_6 were used in the calculation. In the estimation of k_3, it was assumed that the $H\dot{S}O_5$ radicals and not $SO_3^{\cdot-}$ participate in the chain termination reaction, i.e. that $[H\dot{S}O_5]\,[SO_3^{\cdot-}]$, while the rates of the chain termination reactions (2) and (3) (Scheme 5) are equal. The value of k_6 adopted may be too high, but the result of the calculation is relatively insensitive to changes in this rate constant by even one or several orders of magnitude. The principal chain termination reaction is stage (5) of Scheme 5. We did not take into account the possible interaction of HSO_5^- with HSO_3^-, which was regarded in Backstrom's mechanism[101] as the principal route to the formation of SO_4^{2-}. In the mechanism presented, the contribution of this reaction to the overall rate of formation of sulphate ions is much smaller than the contribution of reactions (3) and (4) of Scheme 5. We assume that $[SO_2]_G$ is 10 times greater while $[H\dot{O}_2]_G$, $[\dot{O}H]_G$, and $[H_2O_2]_G$ are 10 times smaller than in the background atmosphere. We note particularly that, if we neglected the NH_3 flux, then not only would we be unable to account for the presence of NH_4^+ in the drops but an appreciable decrease in the final value of $[SO_4^{2-}]$ would have resulted. The results of the calculation are illustrated in Fig. 4. Without over-estimating the importance of this calculation, we may note that it allows the possibility of a chemical explanation of the formation of acid drops at pH→3. The choice between the chemical and absorption mechanisms can be made after determining the accommodation coefficient of H_2SO_4.

It is noteworthy that, as shown by the calculation, a further increase in $[SO_2]_G$ does not lead to appreciable changes in $[SO_4^{2-}]$ and $[H^+]$, i.e. an increase in the amount of SO_2 waste ejected, which increases the volume of precipitated acid rain, should not entail an increase in its acidity. The results of the mathematical modelling of drop processes in contaminated and background atmospheres resorting to experimental data will be described in greater detail in a separate publication by Purmal' and Travin[105], whom the authors thank.

In conclusion, we may note that the rapid reactions of $\dot{O}H$ with HSO_3^- and of $H\dot{O}_2$ with O_2^- in drops necessitate taking into account the loss of OH_G and $H\dot{O}_{2G}$ to the drop when calculating their tropospheric concentrations in the cloud zone. Our estimates have shown that the losses cease to be negligible when the coefficient of the volume saturation of the gas phase by drops is 10^{-6} and less.

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Mathematical modelling in problems of the chemistry of the atmosphere

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ABSTRACT. The characteristics of the mathematical modelling of chemical processes in the atmosphere, their relationship with geophysical processes, their classification in terms of space-time scales, and the sensitivity of the models are examined. The possibilities of modelling the photochemical mechanisms of the reactions of oxygen-, hydrogen-, nitrogen-, sulphur-, and carbon-containing compounds in the background atmosphere and in air in polluted regions and the selection of the parametrisation conditions in conformity with the aims of the given tasks and the hydrometeorological regime are analysed.

The experience gained in the practical use of models of the quality of air in designing a monitoring strategy and measures for the protection of nature is surveyed.

The bibliography includes 133 references.

Contents

I.	Introduction	1024
II.	Characteristic features of the construction of mathematical models for the description of chemical processes in the atmosphere	1025
III.	Classification of models in terms of space-time scales	1026
IV.	Analysis of the sensitivity of the models	1032
V.	Models of chemical reactions of impurities in drops and clouds	1032
VI.	Characteristic features of the mathematical models of the photochemical formation of aerosols	1033
VII.	The use of mathematical models for monitoring the quality of air	1033
VIII.	Conclusion	1034

I. Introduction

Phenomena such as climate warming, the change in the ozone layer, acid rain, the inhibition of plant growth and destruction of forests, and smog phenomena in polluted industrial regions have been attributed to the breakdown of the natural chemical balance in the composition of the atmosphere[1–5]. The appearance of large amounts of toxicants in the atmosphere inevitably affects the ecosystem as a whole[6–9]. An adequate description of the chemical processes occurring in a complex reactor such as the atmosphere is possible only by resorting to mathematical models, which are capable, in conjunction with monitoring systems, of reflecting the entire wide variety of the phenomena and their interaction and permitting an assessment of the consequences of the chemical perturbations of the natural composition of the atmosphere by different sources.

Considerable progress in fundamental research into the atmosphere[10–15], in particular into the modelling of the processes of the dispersion and reactions of the natural and anthropogenic impurities in the atmosphere[16–19], has been achieved in recent years. The advances in chemical kinetics associated with the study of the mechanisms of chemical reactions has made it possible to describe the cycles of reactions of chemicals under natural atmospheric conditions and in the atmospheres of polluted industrial regions. Detailed study of the processes at the level of an elementary chemical step revealed the important role of atoms and short-lived free radicals in processes leading to the transformation of substances[10,11,20,21].

The assemblies of species playing a significant role in the reactions of chemical elements have been combined for convenience into families of O-, H-, N-, S-, C-, Cl-, Br-, and I-containing compounds[10–13]. Organic substances, the mechanisms of the reactions of which have been studied particularly vigorously in recent times in connection with the need to understand the reactions of organic impurities in air over motorways, over forests, and under the conditions of a polluted atmosphere, have been segregated in a separate group[11,12,14]. The experimental data on the chemical kinetics and photochemistry of the gas-phase reactions have been recently surveyed by an Expert Panel within the framework of the IUPAC Subcommittee for Gas-Phase Kinetics, which periodically publishes compilations of kinetic and photochemical data concerning the chemistry of the atmosphere[22,23].

A quantitative description of individual families of reactions, close to the real conditions, is achieved with the aid of mathematical models of different degrees of complexity and with different degrees of detail, depending on the aims of the studies and their practical applications[24–29]. The mathematical models based on data obtained by chemical monitoring using highly sensitive and rapid analytical methods make it possible to approach a solution to problems concerning the prediction of the chemical composition of the atmosphere on both global and local scales.

In the present review, attention is concentrated on the mathematical models used in the study of the photochemical reactions in the atmosphere. This has been done for two reasons. Firstly, the photochemical mechanism of the reactions of substances under the influence of solar radiation is the most common to all the layers of the atmosphere. It establishes the chemical composition of the atmosphere as a whole and its heat balance[2,10,11,13]. Secondly, the mathematical models for the description of photochemical reactions in the atmosphere have been fairly thoroughly developed and a great variety of them are available, which makes it possible to demonstrate the possibilities of mathematical modelling in the

solution of theoretical and applied problems in atmospheric chemistry.

II. Characteristic features of the construction of mathematical models for the description of chemical processes in the atmosphere

The laws of conservation of energy, momentum, and mass, which together with the fundamental rules of thermodynamics and chemistry describe the establishment of atmospheric motions and the transport and transformation of various substances against the background of the latter, constitute the theoretical basis of the mathematical models describing the geophysical and chemical processes in the atmosphere. In terms of mathematics, these are systems of equations for the hydrothermodynamics of the atmosphere (taking into account the transport and transformation of moisture) and systems of equations for transport processes and the reactions of impurities which describe both positive and negative feedback[17]. The complexity of the interrelations between the geophysical and chemical processes in the atmosphere as well as the incomplete knowledge of this field have led to ambiguity in the formulation of problems and in the selection of ways of solving them. The wide variety of approaches to the construction of mathematical models for the transport and transformation of impurities in the atmosphere and the principles governing their practical application have been described in fair detail in the Proceedings of the International Symposium held in 1986 in Leningrad[18].

In order to discover the characteristic features of the physical and chemical phenomena in the atmosphere, an open version of mathematical models is usually employed, in which the elements of the hydrometeorological regime in the atmospheric circulation are assumed to be known and the occurrence of chemical reactions against the background of atmospheric motions is investigated. Three cases are then distinguished depending on the relation between the characteristic chemical and dynamic time scales (t_c, d_d). If $t_c < t_d$ (for example, for short-lived atoms and free radicals), then the chemical reactions can be considered regardless of the atmospheric dynamics. On the other hand, when $t_c > t_d$, the role of dynamics is great (this happens, for example, in the study of trace species such as chlorofluoromethane, carbonyl sulphide, nitrous oxide, etc.). The case where $t_c \simeq t_d$ is most complex and the interpretation of the observations under natural conditions can therefore also be far from unambiguous (for example, for ozone and nitrogen oxides). In order to describe the behaviour (variation of the concentation) of a given impurity and to estimate its residence time in the atmosphere, it is as a rule necessary to carry out a joint analysis of hydrometeorological, physical, and chemical processes.

Analysis of the space-time scales determines the formulation of the problems of atmospheric chemistry which can be arbitrarily divided into the chemistry of the stratosphere, the chemistry of the troposphere, and the chemistry of industrial regions.

The overall structure of models of the transport and transformation of impurities in the atmosphere includes a system of equations of the following type:

$$\frac{\partial c_i}{\partial t} + \operatorname{div} c_i\mathbf{u} - \operatorname{div}_S \mu \operatorname{grad}_S c_i - \frac{\partial}{\partial z}\nu\frac{\partial c_i}{\partial z} + B_i(\mathbf{C}) = f_i, \tag{1}$$

where c_i is the concentration of the ith component at a point $\mathbf{x}$ in space at a time t, $\mathbf{u}$ the velocity vector of the air masses and impurities, μ and ν are the coefficients of the turbulent mixing of impurities in the horizontal (x, y) and vertical (z) directions, $\mathbf{C} = \{c_i(i = \overline{1, n})\}$ the impurity concentration vector, n the number of impurities, $B(\mathbf{C}) = \{B_i(\mathbf{C}), (i = \overline{1, n})\}$ the operator describing the impurity transformation processes, and $f_i(\mathbf{x}, t)$ $(i = \overline{1, n})$ are sources of impurities. The divergence and gradient operators are determined in the usual way in the selected coordinate system. The subscript S denotes operators acting in horizontal directions.

The problem is considered in the region where $D = \{D \times [0, \bar{t}]\}$, where $[0, \bar{t}]$ is the range of variation of the time t, D the region of the spatial coordinates $\mathbf{x} = \{x_\alpha, \alpha = \overline{1, k}, k \leqslant 3\}$, and k is the number of dimensions of the space.

In this case the velocity vector $\mathbf{u}$ can be represented by $\mathbf{u} = \{u_\alpha, \alpha = \overline{1, k}, k \leqslant 3\}$, where u_α is the component in the direction of the coordinate x_α. In the three-dimensional case, one usually employs the designation $\mathbf{x} = (x, y, z)$. The sources $f_i(\mathbf{x}, t)$ $(i = \overline{1, n})$ are specified as the input parameters of the model in the form of functions of spatial coordinates and time. One then takes into account sources of natural and anthropogenic origin.

To complete the description of the model, one specifies the initial and boundary conditions:

$$\text{when } z = Z_S(x, y) \quad R_{1_i}(\mathbf{C}) = f_{1_i}(x, y, t), \tag{2}$$

$$\text{when } z = H \qquad R_{2_i}(\mathbf{C}) = f_{2_i}(x, y, t), \quad i = \overline{1, n}. \tag{3}$$

Here R_{1_i} and R_{2_i} are certain operators and f_{1_i} and f_{2_i} are the sources and sinks of impurities at the $[z = Z_S(x, y)]$ and upper $(z = H)$ limits of the region D. The operators $R_{1_i}(\mathbf{C})$ describe the interaction of the impurities with one another and with the Earth's surface including the exchange processes between air, water, soil, the plant cover, etc., while the operators $R_{2_i}(\mathbf{C})$ describe the behaviour of impurities at the upper limits of the air masses. The descriptions of the operators $B_i(\mathbf{C})$, $R_{1_i}(\mathbf{C})$, and $R_{2_i}(\mathbf{C})$ are specified for each specific problem.

The conditions governing the periodicity of all the functions on the surface of a sphere and, for models designed for a limited area, the conditions governing the concentration field at the lateral boundaries are specified in terms of horizontal variables for the global model. In the vertical velocity, one takes into account the rate of gravitational precipitation of impurity particles which are heavier than air or the rise of particles which are lighter than air at the corresponding height as a result of buoyancy forces.

The first four terms in Eqn. (1) constitute the linear part of the model. The transport and turbulent exchange processes for each substance take place independently of other processes. The operator $B(\mathbf{C})$ is in the general case non-linear, describing the rate of change of the concentrations $\mathbf{C} = \{C_i, i = \overline{1, n}\}$ as a result of chemical and photochemical reactions. Since we are dealing with multicomponent impurities, the number of components n is an input parameter of the model. In practice, n is determined by the model for the transformation of impurities or by the number of substances involved in the reactions.

The hydrometeorological regime in the air masses against the background of which the impurity transport and transformation processes take place is described by the fields of the components of the wind velocity vector $\mathbf{u}$ and the turbulent exchange coefficients $\mu(\mathbf{x}, t)$ and $\nu(\mathbf{x}, t)$. In addition, the temperature, density, and

pressure fields as well as the characteristics of the humidity field, which are in general necessary for the description of the impurity transformation models and for the calculation of the reaction rates, are specified parametrically. The parameters of the hydrometeorological regime are usually assumed to be specified. Naturally, such separation of hydrothermodynamic and chemical processes in the model is extremely arbitrary and can be acceptable for relatively short time intervals and only for the sake of the simplification of the description of the overall structure and content of the impurity transport and transformation models.

The point is that in the general situation one cannot do without negative feedbacks. Many of the impurities belong to the class of optically active substances and influence the radiation processes in the atmosphere, while some influence also the moisture transformation processes, acting, for example, as condensation nuclei. All this leads to changes in the thermal and humidity-dependent processes in the atmosphere and ultimately to changes in hydrometeorological regime, i.e. in the velocity fields and in the turbulent exchange. The problem consists in the evaluation of the characteristic time scales of such negative feedbacks and of the intensity of the changes in the background processes determined by the effects of their negative feedbacks.

As a result of the modification of the formulation of the problem defined by Eqn. (1)–(3), different types of models are obtained. These modifications are determined by the following features:

the way in which the parameters of the hydrometeorological regime — the turbulent exchange models — are specified;

the procedures used to describe the boundary conditions and sources — the interactions of impurities with the underlying surface;

the choice of the space-time structure of the region, i.e. the dimensions of the problem and the hypotheses concerning the nature of the dependence of the investigated phenomena on the variables x, y, z, and t;

the procedure used to describe the impurity transformation operators;

the space-time scales of the phenomena investigated — the procedures used for a discrete description of the models and the methods of their application on a computer;

the combinations of the variants described.

An important stage in the construction of numerical models is the discrete specification of the initial problems in a differential formulation. Different procedures for such discrete specification are used nowadays — finite-difference, finite-elementary, spectroscopic, spectroscopic-difference, and their various combinations. The choice of a specific scheme is determined by the ratios of the space-time scales of the processes taken into account in the model. Together with models with rigorously determined formulations, models based on statistical modelling methods (the Monte Carlo method) are being developed.

III. Classification of models in terms of space-time scales

In relation to time, the model can be stationary or non-stationary, while in relation to spatial variables we have "point", one-dimensional, two-dimensional, and three-dimensional models.

In point (or box) models, there is no description of transport processes. Such models arise when the characteristics of the composition of the atmosphere are averaged out on the assumption of spatial homogeneity and account is taken of only stationary and non-stationary impurity transformation processes. They are convenient for the interpretation of laboratory experiments, for example in smog chambers[30–33]. Chemical processes, including all the elementary stages, are studied in detail in such models. Integration of a short time interval is used in the study of the kinetics of the reactions of reactants and products. Comparison of the results of such modelling with the results of measurements sometimes stimulates a specific search for new processes, the allowance for which would promote the reconciliation of the results of modelling and experiments[34].

One-dimensional models are usually employed when the changes in the impurity concentration fields as a result of transport and turbulent exchange are significant mainly in one direction, while in other directions once can restrict the treatment to the assumption of uniformity. This occurs, for example, in the solution of problems of the stratosphere in connection with the study of vertical motions and of problems of the boundary layer of the atmosphere over a homogeneous area of the Earth's surface[25,35–43].

1. Photochemical models of the stratosphere

The chemistry of the stratosphere is relatively simple and is described in terms of compact models. Usually 20–30 chemical species, 100–200 reactions, a temperature of 200–300 K, and a pressure of 1–100 torr are involved. The most important aspect of these problems is the photochemistry of ozone[21]. Here it is necessary to take into account four groups of species[13]: (1) "odd" oxygen O_3, $O(^1D)$, and $O(^3P)$ whose reactions are based on the classical Chapman cycle; (2) long-lived gases of tropospheric or biospheric origin, such as H_2O, O_2, N_2, CO, CH_4, H_2, CH_3Cl, CF_2Cl_2, COS, etc; (3) short-lived radicals, for example OH, HO_2, and Cl, participating in catalytic ozone decomposition cycles (we may note that allowance for these has made it possible to eliminate a number of problems concerning the ozone balance[11]); (4) the products of the reactions of short-lived radicals such as HNO_2, HNO_3, HO_2NO_2, $ClONO_2$, H_2SO_4, and H_2O_2. The most important criterion of the adequacy of such models is the agreement between the calculated and measured concentration profiles of the species most sensitive to variations in the input parameters of the models. In terms of such models, one investigates either the diurnal changes in the short-lived species or one calculates the height profile of the concentrations of the molecules averaged over long time (t) intervals. The increased interest in the chemistry of ozone in the stratosphere has led in recent years to the search for additional chemical processes which may occur in a polluted stratosphere. Thus, in order to account for the observed decrease in the amount of ozone in polar regions[26], it is necessary to resort to heterogeneous reactions involving ozone.

The attempts to understand further and to predict the changes in the content of impurities in the stratosphere under the influence of anthropogenic perturbations are nowadays based mainly on two-dimensional models which are capable of modelling the changes in concentrations as a function of two spatial variables — height and one horizontal dimension, as well as the season and the time of day. The spatial-temporal resolution and the algorithmic possibilities of such models are determined by the speed and the size of the memory of the computers employed.

Two-dimensional models are more realistic than one-dimensional models, but they too describe only individual features of the investigated phenomena. Since in recent years appreciable progress has been observed in the method for the determination of certain impurities in the atmosphere and of their dynamics, it has become

possible to compare the calculated and measured concentrations. This has stimulated a rethinking of the ideas concerning the role of certain reactions in the atmosphere.

Three-dimensional models are most consistent with the conditions in the real atmosphere. They usually combine the species transport processes, the interaction with radiation, and the photochemical reactions of the species and constitute an effective instrument for discovering the characteristic features of the establishment of the concentration profiles for impurities such as O_3, CO, CO_2, nitrogen- and sulphur-containing substances, etc. and for the determination of the level and consequences of the anthropogenic stimuli[45–48]. In three-dimensional models, much attention is devoted to their ability to describe diurnal and seasonal changes in concentration fields. Some models make it possible to calculate rapid chemical transformations of impurities on the assumption of slow changes in other parameters under the influence of external conditions. Conversely, others do not permit calculations for rapid processes but do make it possible to take into account the types of sources, sinks, and the transfer and transport of long-lived impurities. The decisive external parameters under these conditions are the concentrations of short-lived species, for example, the OH radical[13]. Models in which large averaging scales in space and time are postulated are usually employed for climatic predictions.

Much attention has been devoted recently to the development of three-dimensional models for the study of the chemistry of the polluted atmosphere of industrial regions[44–61]. The multiplicity of approaches to the construction and application of such models have been tried. Thus models of the dispersal of impurities arising from powerful sources take into account the transport processes on a regional scale but neglect the details of the chemical transformations. Local models of the "quality of air" include the chemistry of atmospheric contaminants usually with parameterised decriptions of the transport processes. Such models are as a rule designed for ecological predictions on a regional scale (including different countries).

Table 1. Classification of the models in terms of characteristic space-time scales of the processes and typical problems solved with the aid of the models.

Horizontal scale, km	Vertical scale, km	Specific features of ecological problems
1–10	1–5	Influence of open-cast mining, chemical and aerosol methods in agriculture, and large industrial units on the environment
10–100	5–10	The microclimate and pollution of urban atmospheres
10–100	10–20	Effect of powerful anthropogenic heat sources on the environment with evolution of polluting impurities
100–1000	10	Environmental protection problems for large territorial-industrial complexes and influence of large hydrotechnical units on the hydrothermodynamics of the atmosphere
1000–10000	10	Studies on the cyclogenesis and the long-range transport of impurities
Global	10–30	Energy and mass exchange in climatic system and the global transport of impurities in the atmosphere

Questions concerning allowance for feedback effects, which arise in the joint consideration of chemical processes together with processes involving the hydrothermodynamics of the atmosphere may be regarded as little developed aspects of three-dimensional models. The construction of complex models greatly complicates the formulation of the problem and requires the solution of the problem of a self-consistent description of processes on different space-time scales. Thus the specific problem and the range of phenomena considered dictate the choice of the structure of the model, its discrete analogues, and the methods of parametrising chemical and physical factors. Table 1 presents a classification of models in terms of space-time scales, which provides an idea about certain possible combinations of hydrothermodynamic models with models of the chemical transformations of mixtures.

The technology of the modelling of chemical processes in the atmosphere consists of several stages, which are common to the majority of models. The structure of numerical algorithms for the application of the model on a computer depends in many respects on the choice of a particular transformation mechanism (photochemical mechanism, reactions in drops, heterogeneous reactions, combustion processes), in order to take into account in the model of the atmosphere, and on the degree of its development.

The modelling of a photochemical process consists of the following stages.

1. The formation of a data base of reaction rate constants and establishment of a system of kinetic equations.
2. Determination of the dependence of the rate constants on temperature, pressure, intensity of solar radiation, moisture, etc.
3. Establishment of a system of differential equations describing the kinetics of the processes.
4. Analysis of the characteristic time scales of the chemical reactions and estimation of the lifetimes of the species taken into account in the system of equations.
5. The study of the properties of the solution of the system of differential equations for specified reaction rate constants and initial concentrations of impurities.
6. Analysis of the sensitivity and the stability of the defining equations with respect to variations in the input parameters.
7. The selection of a scheme for the integration of the system of equations for the transformation of impurities. The study, on the basis of an analysis of the time scale and of the sensitivity of the model to variations in the input parameters, of the possibility of the "contraction" of the system of equations in terms of a specified criterion with retention of the material balance and of the properties of the solution.
8. Interpretation of the results of numerical modelling and their comparison with data derived from experimental studies and measurements under natural conditions. If necessary, the parameters of the models can be identified on the basis of factual information.

It is noteworthy that problems concerning the mathematical modelling of chemical processes occurring in the atmosphere are of independent interest from the standpoint of computational mathematics[17]. The systems of differential equations for their description are as a rule non-linear. The number of reactions in real problems may reach several hundreds and they occur at each point in a three-dimensional region against the background of relatively slow hydrothermodynamic circulation of the atmosphere. The reaction rate constants differ by several orders of magnitude. The systems of defining differential equations can be classified in terms of their properties as so called "stiff" systems. All the foregoing factors indicate the complexity of the solution of such problems on modern computers.

One of the convenient methods for the algorithmic application of the models is the cleavage method. The method is interesting because it makes it possible to model processes over a short time

interval in such a way that in one stage the calculation of transport proceeds in parallel and independently for each species throughout the region, while in another the set of systems of equations describing the transformation of the impurities at each point in space is solved for all the species simultaneously and independently of their solution at other points. Such organisation of the model makes it possible to reconcile the characteristic scales of different processes and to facilitate significantly the solution of problems of the parametrisation of impurity transformation processes when their characteristic time scales are short compared with the steps used in the specification of the model in a discrete form as a function of time. The computational algorithms then obtained are simple to apply and economical as regards the number of arithmetical operations.

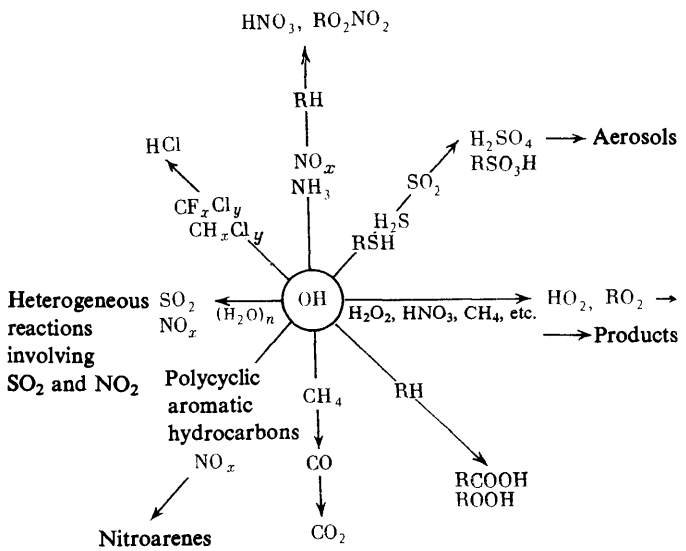
2. Photochemical models of the troposphere

The chemical models of the troposphere are much more complex than the stratospheric models for a number of reasons. Firstly, much more complex impurity transport and diffusion processes take place in the troposphere, in which turbulence, characterised by a marked spatial-temporal variability, plays an important role. Secondly, owing to filtration by the ozone layer, only light at wavelengths longer than 290 nm penetrates into the troposphere. The primary photochemical processes therefore take place in the troposphere with different rate constants. Among them, the reactions involving the photolysis of ozone and of nitrogen oxides with formation of atomic oxygen are the most important. The reaction of $O(^1D)$ with the admixtures of water vapour in the atmosphere, i.e.

$$O(^1D) + H_2O \rightarrow 2OH$$

to form the hydroxyl radical OH, plays a key role in the chemistry of the troposphere (Scheme 1)[10-12]:

Scheme 1



The quantitative and qualitative composition of the impurities in the troposphere is incomparably more varied than in the stratosphere. There are considerable differences between the compositions of the atmosphere in the layer near the Earth's surface over different regions. Fig. 1 compares the concentrations of impurities typical for the air of unpolluted and industrial regions. The horizontal lines indicate the levels of the maximum permissible concentrations (MPC) recommended as health norms for quality of the atmosphere. Fig. 1 shows that the concentrations of the impurities vary by several orders of magnitude in both unpolluted and polluted atmospheres. The chemical compositions of the impurities in air over the oceans, forests, and desert are usually significantly different.

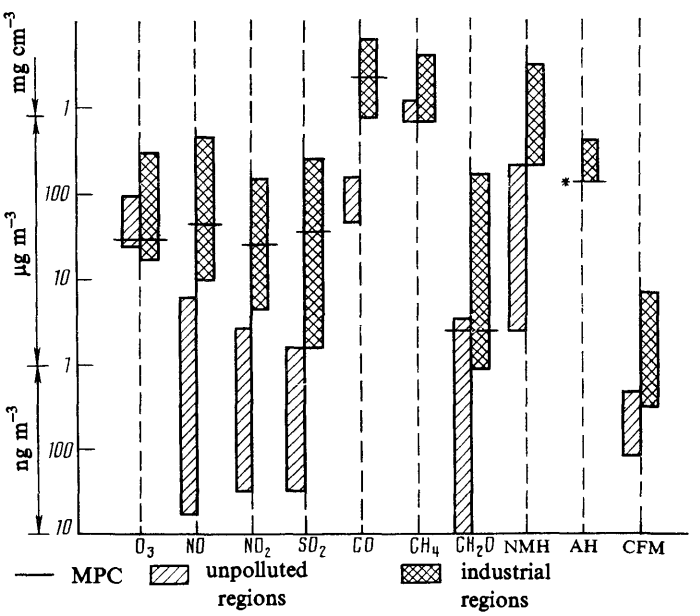


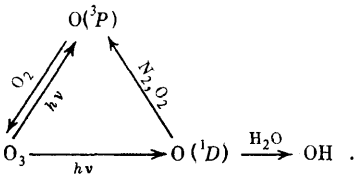
Figure 1. Concentrations of typical impurities in the air of unpolluted and industrial regions: NMH—non-methane hydrocarbons; AH—aromatic hydrocarbons; CFM—chlorofluoromethanes. *The maximum permissible concentration (MPC) of xylene, the most widely distributed aromatic hydrocarbon in cities, is indicated[8,14,15,62,63].

The concept of the "background" atmosphere, whose composition is recommended as a reference standard for the estimation of air quality, has therefore been adopted. In a polluted atmosphere, one uses for this purpose the values of MPC which can be adopted by convention as a norm of the "purity" of the polluted air. The modelling of chemical processes in the background and polluted atmospheres in different regions therefore constitutes problems with different degrees of complexity and the input parameters for their solution must be based on data for the composition of air in both the background atmosphere and the polluted atmosphere of a particular region.

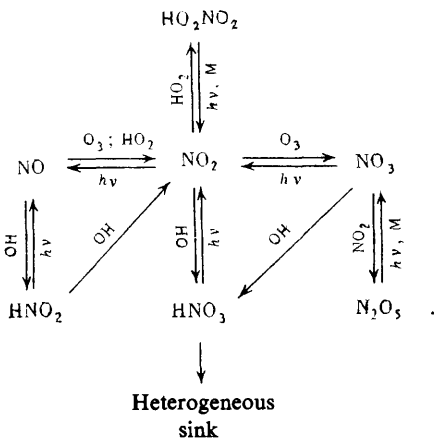
(a) The background troposphere. The chemistry of the background troposphere is in many respects similar to the chemistry of the stratosphere. Thus the same reactions (Scheme 2–4) take place in the families of the O-, N-, S- and C-containing compounds as in the stratosphere, but the number of possible reaction pathways is greater and additional species appear as a consequence of the greater variety

of the impurities and of their concentrations in the troposphere. We may note that the halogens are actively involved in the chemical reactions occurring in air over the seas[10,13,49,63].

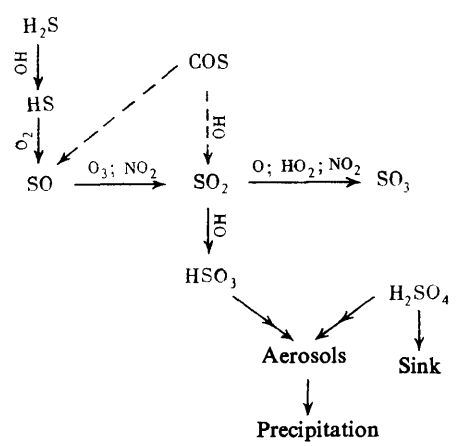
Scheme 2



Scheme 3



Scheme 4



Organic compounds occupy a special place in the photochemistry of the troposphere. Whereas only a few of relatively stable substances at low concentrations (for example, chlorofluoromethanes, carbonyl sulphide) penetrate into the stratosphere from the Earth, in the troposphere the situation is significantly different. An insignificant increase in complexity compared with the stratosphere is observed only in the atmosphere over the seas. Owing to the presence of terpenes in the air over forests, the scheme of the transformations of the impurities is supplemented by the reactions of terpenes with ozone and nitrogen oxides[63,64].

Hydrocarbons in general differ sharply in their reactivities and reaction mechanisms from other compounds. Their potential capacities to generate secondary contaminants are also not the same.

In such situations, it is necessary to take into account the multicomponent nature and the pronounced spatial-temporal non-uniformity of the distribution of these compounds. In the study of the photochemistry of the troposphere in the 1970s, the consideration of individual organic compounds was therefore replaced by the study of multistage photochemical mechanisms[32]. Proof of the validity of this treatment of atmosphere chemistry was obtained in numerous kinetic laboratory experiments and in smog chambers both in the investigation of simple mixtures and for real waste products[30,53,65–67].

Analysis of the results obtained in carrying out the programme of the Global Tropospheric Experiment[68–70] in order to test the existing photochemical models confirmed in many respects the validity of the ideas about the photochemistry of the atmosphere and has raised a number of problems requiring a more detailed study. Investigations of the atmosphere over polluted regions in order to develop a strategy for the monitoring of air in the atmosphere using mathematical modelling for such purposes belong to the range of studies of greatest current interest.

(b) Models of the atmosphere over polluted regions. The monitoring of the composition of the atmosphere over polluted regions revealed a series of factors which require interpretation, especially under smog conditions. Apart from carbon monoxide, nitrogen oxides, sulphur dioxide, and hydrocarbons, which are present at increased concentrations in automobile transport exhausts, in the flames generated in thermal electric power stations, and elsewhere, substances which are not characteristic of the primary industrial waste were also recorded, for example, peroxynitrates, organic sulphur- and nitrogen-containing compounds, organic acids, and peroxides. Furthermore, anomalies were noted in the diurnal variation of the concentrations of ozone[11,12,15,71]. This shows that secondary photochemical oxidants are formed in all kinds of photochemical smog[11,26,51,53,57].

Models of the chemistry of the atmosphere in areas with an increased anthropogenic input, characteristic of industrially developed regions, make it possible to describe the dynamics of the appearance and development of smog situations. As an example, we shall describe briefly one such model of the transport and transformation of impurities against the background of the hydrometeorological regime of an industrial region[17,72,73]. Its structure is typical for models of this class known in the literature[18,19]. Two versions of calculations are usually employed—in the linear and non-linear approximations, and the model is as rule tested in relation to the most typical waste ejected into the atmosphere in industrial regions—SO_2, NO, NO_2, CO, CH_4, and CH_2O. The chemical reactions of these compounds are initiated by sunlight which results in the activation of photoactive molecules, for example, SO_2, NO_2, and CH_2O. Atoms and free radicals as well as certain products together with the initial waste participate in the intermediate stages of the chemical reactions.

The linear approximation is based on the application of the method of quasi-stationary concentrations of active species (atoms, free radicals, and electronically excited molecules). The reaction rate constants used in the calculations are available in familiar handbooks on atmospheric chemistry[22,23,74]. Apart from atoms and free radicals, the photochemical reactions result in the appearance and accumulation of products which were not present in the initial

waste, for example, nitric, nitrous, and sulphuric acids as well as hydrogen peroxide.

The non-linear model is used in calculations for the set of reactions of nitrogen, sulphur-, and carbon-containing compounds most characteristic of the atmosphere in industrial regions.

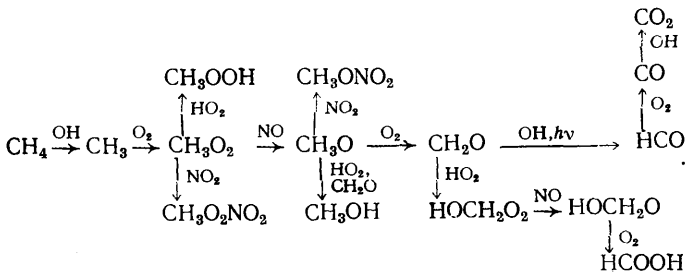
In mathematical models, there is a possibility of different modifications in the descriptions of the mechanisms of the transformation of organic compounds. A classification of hydrocarbons into three groups was adopted in 1977: alkanes, alkenes, and aldehydes[32]. Aromatic compounds have not been considered separately hitherto. Among all these compounds, the photochemistry of methane has been studied in greatest detail in view of its possible climatic consequences[2,75,76].

For these purposes, a simplified scheme of the reactions of methane is usually considered:

$$CH_4 \rightarrow CH_2O \rightarrow CO \rightarrow CO_2 .$$

It is employed, for example, in global models in estimating the greenhouse effect. High concentrations of CH_4, CH_2O, and CO and more complex combinations of impurities in the polluted atmosphere require a more complete methane oxidation scheme (Scheme 5). This is necessary in the assessment of the overall toxicity of the air in polluted regions. Analysis of the results obtained within the framework of both simplified and complete methane oxidation schemes[73] revealed the necessity to increase the number of methane reactions considered under the conditions of polluted air. The complete computational scheme takes into account about 200 elementary stages, while in the simplified scheme the number of such stages is only 40.

Scheme 5



As a consequence of the non-linearity of the problem being solved, it is of interest to elucidate the influence of the level of waste products on the final chemical composition of the contaminated air. Certain examples of such calculations are presented below. In the first of these (Fig. 2), the amount of CH_4 waste varies over three orders of magnitude. It is found that the increased amount of methane emitted is accompanied by a non-linear growth of the concentrations of peroxides, formic acid, and carbon dioxide. The dependence of the yield of products on the amount of formaldehyde waste is more complex (Fig. 3). The concentrations of many intermediate and final products [$O(^3P)$, O_3, OH, HO_2, NO_3, CH_3O_2, H_2O_2, CH_3OH, CH_3OOH, HCOOH, HNO_2, HNO_3, HO_2NO_2 (Fig. 4)] are influenced by the level of waste nitrogen dioxides. The dependence on NO_x is non-linear. This is manifested in two ways: the content of the acids HNO_2 and HNO_3 increases and that of other products—peroxides, organic acids, and peroxynitrate—falls. The concentration of ozone changes little under these conditions, because only the NO_2/NO ratio is important in determining it.

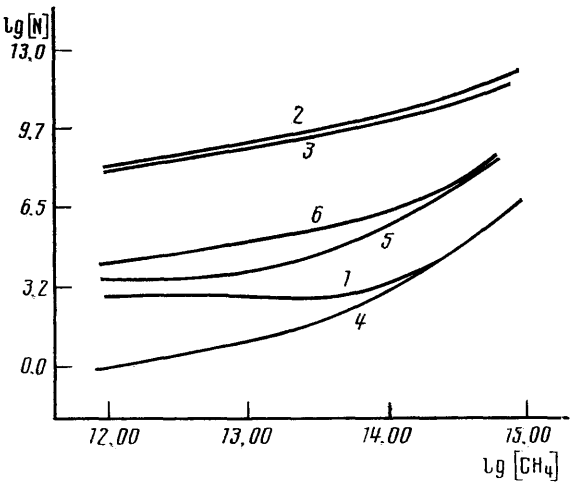


Figure 2. Logarithmic dependence of the formation of H_2O_2 (curve *1*), CH_2O (curve *2*), CO (curve *3*), CH_3OOH (curve *4*), HCOOH (curve *5*), and CO_2 (curve *6*) on the methane concentration (cm^{-3}) for t = 12 h (the accompanying concentrations are 10^{11} cm^{-3} for NO_x and 2.6 × 10^{11} cm^{-3} for O_3) [73].

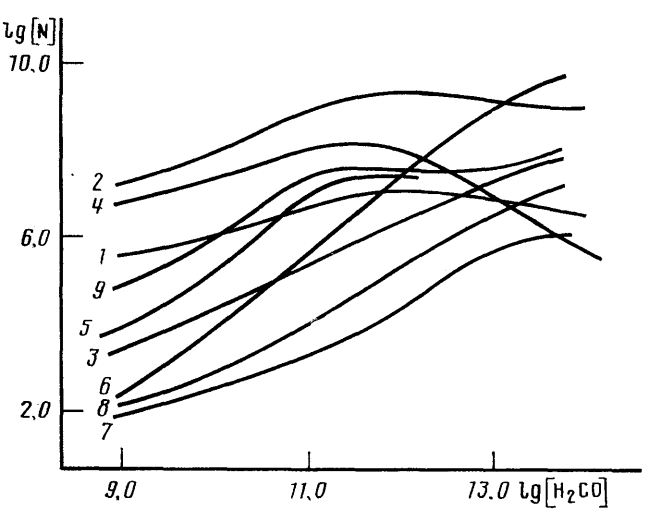


Figure 3. Sensitivity of the OH (curve *1*), HO_2 (curve *2*), CO × 10^{-7} (curve *3*), CH_3O_2 (curve *4*), CH_3OOH × 10^{-3} (curve *5*), HCOOH × 10^{-4} (curve *6*), CH_3ONO_2 × 10^{-4} (curve *7*), HO_2NO_2 × 10^{-5} (curve *8*), and CH_3OH (curve *9*) concentrations to variations in the amount of formaldehyde on the logarithmic scale for t = 12 h (accompanying concentrations 10^9 cm^{-3} for NO_x and 3 × 10 cm^{-3} for CH_4) [73].

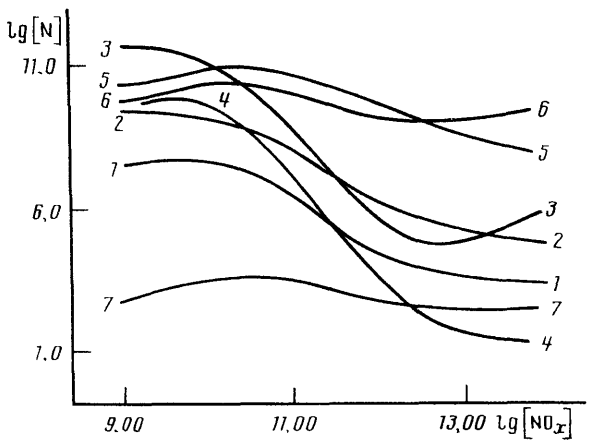


Figure 4. Sensitivity of the CH_3O_2 (curve *1*), HO_2 (curve *2*), H_2O_2 (curve *3*), CH_3OOH (curve *4*), HCOOH (curve *5*), HO_2NO_2 (curve *6*), and CH_3O (curve *7*) concentrations to variations in the amount of NO_x on a logarithmic scale for t = 12 h (accompanying waste products 2 × 10^{13} cm^{-3} for CO, 3 × 10^{13} for CH_4, and 2.4 × 10^{11} cm^{-3} for CH_2O) [73].

Fig. 5 shows that under polluted conditions, the diurnal variation of the concentration of OH radicals did not follow exactly the diurnal movement of the sun in the chemistry of both the stratosphere and the background troposphere—its maximum may be observed also at other times in the morning and in the evening.

Thus consideration of the photochemical oxidation of methane alone in a polluted atmosphere shows how great is the increase in the complexity of both the problem itself and of the conclusions reached on its basis and of their interpretation. Fig. 6 presents an example of such a calculation under urban conditions.

Experience has shown that one cannot transfer mechanically the results of calculations, obtained using a model adapted to a particular region, to other regions. The marked non-linearity of the process (i.e. the dependence on the concomitant impurities, for example nitrogen oxides) does not allow the fitting of simple relations to its rate.

The photochemical model was developed further in the 1980s when a data base for non-methane hydrocarbons was created, which made it possible to introduce the latter into the mathematical models for different levels[28,76–81]. As a consequence of this, the degree of understanding of the principal features of the dynamics of photochemical smog increased. A special place has been assigned recently to the chemistry of the nighttime atmosphere as an after-effect of the daytime photochemistry. In these processes, a leading role is attributed to the NO_3 radical, whose maximum concentrations are observed in the atmosphere after sunset[22].

Since the majority of the models involve very laborious computations, one usually endeavours to simplify as far as possible the schemes for the chemical reactions of organic impurities. It is noteworthy that, before simplifying the reaction scheme, it is desirable to carry out calculations within the framework of the most complete scheme and to make sure with the aid of tests that the simplified scheme reproduces the principal results in conformity with the aims of the investigations.

Calvert and Madronich[79] recently examined the detailed chemical mechanism of the oxidation of hydrocarbons in the atmosphere. It included 26 alkanes (C_1-C_8), alkenes (ethylene and propene), aromatic hydrocarbons (benzene, toluene, and xylenes), and terpenes (isoprene and α-pinene). It was shown that, in the absence of nitrogen oxides and in the presence of NO_x at appreciable concentrations in the atmosphere, the oxidation products are significantly different. A rigorous specificity of the products, their concentrations, and their lifetimes is expected for each class of hydrocarbon depending on the conditions, which may serve as a useful indicator of the behaviour of air masses as a function of time.

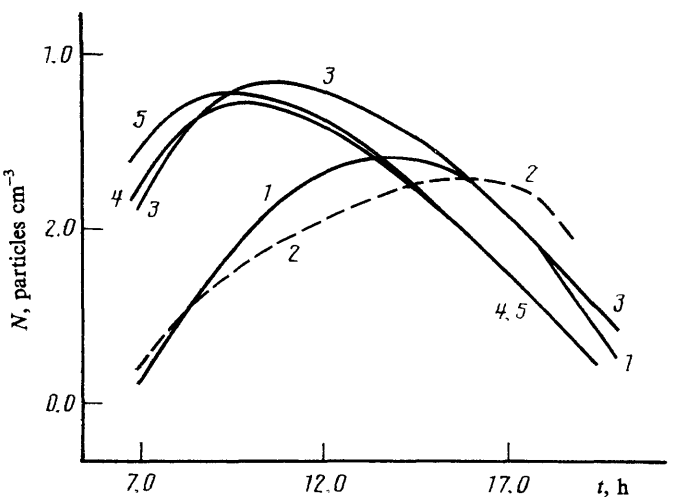


Figure 5. Diurnal variation of the concentrations of the hydroxyl radical OH as a function of the NO/NO_2 ratio (accompanying concentrations 3 × 10^{13} cm^{-3} for CH_4, 2 × 10^{13} cm^{-3} for CO, and 2.4 × 10^{11} cm^{-3} for CH_2O): *1*, [OH] = 0.5 × 10^{-6} cm^{-3} (10^{14} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *2*, [OH] = 2 × 10^{-6} cm^{-3} (10^{13} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *3*, [OH] = 0.4 × 10^{-5} cm^{-3} (10^{12} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *4*, [OH] = 3 × 10^{-6} cm^{-3} (10^{11} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *5*, [OH] = 0.8 × 10^{-6} cm^{-3} (10^{11} cm^{-3} for NO, 10^{11} cm^{-3} for NO_2). {Note by Ed. of Translation: all exponents for [OH] should be positive not negative}.

Another aspect of the chemistry of organic substances in the atmosphere was developed by Atkinson and co-workers[74,77,78]. Comparison of the reactivities (rate constants for the reaction of the OH radical) with the physicochemical properties of organic molecules (ionisation potentials, electrophilic substitution constants, etc.) yielded empirical relations for the calculation of the rate constants for reactions of compounds of different classes with free radicals and ozone. Correlations were discovered between the rate constants for reactions occurring between the OH radical and $O(^3P)$ and also between the NO_3 radical and ozone. This approach makes it possible to estimate the rates of reactions and the lifetimes of many organic compounds and their homologues in the atmosphere and to formulate the principal schemes for the reactions of organic impurities in a polluted atmosphere.

Theoretical studies in the field of tropospheric chemistry of organic compounds have served as a basis for the estimation of the potential toxicity of the entire set of impurities. They are useful in the consideration of pathways leading to the decomposition of substances, for the estimation of their lifetimes in the troposphere, and for the possibility of the appearance and further transformation of secondary products.

IV. Analysis of the sensitivity of the models

The study of the sensitivity of the models to variations in the input parameters and in the rate constants for individual reactions is an essential stage of numerical modelling. It includes the calculation of the partial derivatives of a specified set of characteristics and the estimation of the changes in the functions of state of the model process in terms of the investigated parameters. Here several approaches are used, which make it possible to elucidate the relative significance and the degree of uncertainty in individual stages of the complete scheme, the possibility of its simplification, and also the trends in the development of the principal relations[67,76,83–91]. Such approaches include the direct modelling method, methods based on the solution of variational problems, variational methods using coupled problems, and modelling of the response of the system to specified perturbations.

The simplest and frequently employed procedure is the direct modelling method. It is based on repeated solutions of the defining system of equations with variation of the input parameters. However, repeated solutions become impractical in complex systems with many parameters.

The principal uncertainty in the photochemical mechanism involves the estimation of the rate of photolysis of compounds under real conditions. A clear example is provided by the photolysis of acetone. It was found that in the atmosphere the quantum yield of this reaction is only 0.08–0.15 [69] instead of 1, obtained under laboratory conditions[92]. Demerjian et al.[92] tabulated certain data in the photolysis of a number of molecules as a function of the latitude and the zenithal angle under real atmospheric conditions, but the absorption cross-sections of the molecules and the quantum yields of the photochemical reactions of many compounds have not yet been adequately investigated. The uncertainty is enhanced by the hydrometeorological conditions, for example, the cloud cover.

Whereas the rate constants for reactions involving inorganic compounds have been studied in fair detail, as regards reactions with organic impurities there are considerable uncertainties both in the rate constants and in the products themselves. In 1979, Seinfeld and co-workers[83] analysed the uncertainties in the photochemical mechanism and outlined the priorities in their investigations. Over ten years, there has been considerable progress in these fields: the reactions of ozone with alkenes and the products formed under these conditions were investigated in detail and the parameters of the formation and decomposition of peroxynitrates were refined. In the field of the reactions of aromatic compounds in the atmosphere, qualitatively new and important information has appeared[11,12,23,71,77,93]. The progress which has occurred in the measurement of photochemically active impurities in the atmosphere has made it possible to determine with greater accuracy the initial parameters of the models[68–71].

Analysis of the sensitivity and uncertainty of individual stages of the complete reaction scheme is a useful aid to the formulation of experiments and identification of the parameters exerting the greatest influence on the quality of the prediction. The "counter species" technique has been used[28] for the analysis of complex mechanisms with a large number of stages which makes it possible to test the internal self-consistence of the complex reaction mechanism under different conditions.

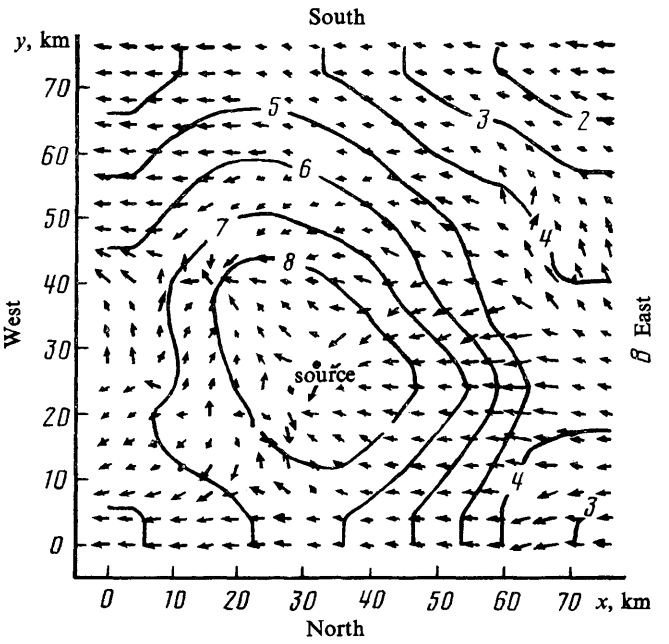


Figure 6. Contours for the variation of the concentrations (continuous lines) of hydrogen peroxide H_2O_2 (on a logarithmic scale) and of the vector field $\mathbf{V} = |V^2 + U^2|$ (arrows) for $t = 12$ h under urban conditions[73].

Studies on the sensitivity of different schemes used in models have thrown light on many questions, for example, on the contribution of aldehydes and aromatic hydrocarbons to the conversion of NO into NO_2, and have made it possible to compare several versions of the schemes describing the system and to formulate the principles of the arrangement of hydrocarbons in groups without prejudicing the quality of the prediction.

V. Models of chemical reactions of impurities in drops and clouds

One of the serious global problems is the formation of acid residues as a consequence of the pollution of the atmosphere by gaseous impurities, which lead to the formation of acid products—the inorganic acids H_2SO_4, HNO_2, and HNO_3, and organic acids, for example HCOOH. Recently the problems of the modelling of such processes have been attacked vigorously[76,94–97]. The gas-phase photochemical reactions examined above precede the acidification reactions and the alteration of the chemical composition of drops. In these models, it is essential to consider in addition the

processes involved in gas–liquid phase equilibria[11,98] and to take into account the possibility of the occurrence of heterogeneous and liquid-phase reactions. For example, in the interpretation of the results of observations in nature for the content of sulphate in precipitates, it proved insufficient to examine only the gas-phase transformations of sulphur dioxide into sulphates with subsequent dissolution and the concept of the chain mechanism of the oxidation of sulphur dioxide in the liquid phase was therefore invoked[99].

The oxidation of NO_2 to HNO_3 in clouds is now considered not only from the standpoint of photochemistry but to a large extent the idea of the reactions of nitrogen oxide in the dark, the so called "night chemistry"[82,97], is also invoked.

Overall, mathematical models throw light on the characteristic features of the formation of acid deposits and their transport processes on both global and regional scales and reveal the possible ecological consequences of these precipitations, for example, the causes of the large scale destruction of forests[3,5].

It is noteworthy that a specific feature of the construction of these models involves the need to build into the model the occurrence of microphysical moisture transformation processes in the atmosphere, self consistent in terms of space-time scales, which itself constitutes a fairly complex physico-mathematical problem.

VI. Characteristic features of the mathematical models of the photochemical formation of aerosols

Phenomena in the climatic systems such as the existence of an aerosol layer is the upper troposphere (for example, the Junge layer) and the decrease in the transparency of air in regions with increased gas-phase pollution are associated under certain conditions with aerosol formation processes under the influence of light[4,11].

The precursors of the relatively involatile products (stimulators of the formation of aerosols) are gas-phase photochemical reactions whose modelling was considered above. The modelling of aerosol formation is therefore a natural development of the models of the transformation of impurities designed to follow the sections of geochemical substance transformation cycles occurring in the atmosphere from the instant of their formation to the instant of their disappearance, because the concentrations of impurities in air are a result of a dynamic equilibrium between their sources and sinks.

For the modelling of the kinetics of the formation of atmospheric aerosols and the establishment of their particle dimensions and chemical composition, it is necessary to take into account the chemical processes leading to the appearance of aerosol products, the transport of gases to the surfaces of the particles, the appearance of new particles as a result of nucleation and coagulation, and equilibrium between the particles and the local gas composition of the medium[11]. The key problems in the modelling of the evolution of the urban aerosol have been solved in a series of studies[52,58,100–105]. The combination of such a model with a three-dimensional model of atmospheric dynamics has made it possible to compare the results of calculations with measurements in nature. The model predicts the daytime and nighttime compositions of the inorganic aerosols for different humidities and permits the estimation of the influence of volatile organic components. For example, it has been concluded that the formaldehyde impurity in clouds inhibits the formation of sulphates and stimulates the formation of formic acid[106]. A sectional model of aerosol dynamics has been developed[107] and the results of modelling have been compared with the results of experiments carried out in smog chambers.

VII. The use of mathematical models for monitoring the quality of air

This section presents certain examples of the application of mathematical models using the photochemical mechanism in the development of a strategy for monitoring the quality of air.

The involvement of sulphur dioxide in the photochemical mechanism has been analysed[53,108]. Determinations, under natural conditions, of the structure and evolution of a plume which contains SO_2, NO_x, and hydrocarbons are inherent in the model taking into account both the photochemistry and the transport processes of these compounds. The rate of conversion of sulphur dioxide into sulphates usually observed in a polluted atmosphere increases from 1–4% per hour (in plumes with a high content of hydrocarbons) to 12–13% per hour. Comparative analysis of the results of measurements and calculations yielded a satisfactory explanation of the sharply rising rate of oxidation of SO_2. It is attributed to the notable influence of hydrocarbons on the transfer of the chain reaction from hydroxyl radicals to peroxy-radicals. It is to be expected that this mechanism can lead to an increase in the rate of reaction of SO_2 to 40% per hour[99].

An especially large amount of attention has been devoted to the elucidation of the problem of the formation of ozone in the atmospheres of polluted regions[12,55,60–62,89,108]. This is due to the fact that ozone belongs to the class of the most significant indicators of air quality and is a representative measure of the secondary pollution of the atmosphere as a result of photochemical reactions[44,45,108–113].

Models corresponding to different levels are used to investigate the chemistry of ozone. Thus the dependence of the concentration of ozone on the ratio $[HC]/[NO_x]$ was investigated in a study[56] where twelve hydrocarbons (HC) were considered. It was found that, for low values of this ratio, the nature of the hydrocarbons themselves is important, while for high values the formation of ozone is limited by the concentration of nitrogen oxides. In another model[55], account was taken of 37 hydrocarbons, 169 species, and 320 reactions. Here attention was concentrated on the characteristic features of the hydrometeorological regime in the atmosphere and on different concentrations of the gases in the sources of pollution. The contribution of individual sources and of different classes of compounds to the formation of ozone was estimated. It was concluded that the exhausts from automobile transport is the most important source.

A regional model, whose development was initiated by the observation of anomalous concentrations of ozone in the atmospheres of polluted regions, constitutes the basis of a strategy for the monitoring of exhaust waste products in the USA. It describes the dynamics of atmospheric and chemical processes on different scales—from global to local. The content of ozone and its diurnal variation are being predicted and the sources (ozone precursors) not taken into account hitherto are being discovered. The very detailed specification of the model helps in its employment for practical purposes on a regional scale[44,45].

A model proposed by Thompson et al.[89] is devoted to the problem of the chemistry of ozone in the troposphere. Here emphasis is laid on the interrelation of the consequences of pollution by methane, carbon monoxide, and nitrogen oxides. It was shown how specific features of the injection of one impurity lead to changes in the concentration of O_3, which depends on the level of the remaining impurities. A hybrid model has been developed[108] for the estimation of the behaviour of waste products from different point sources.

It combines the treatment of data obtained in measurements under natural conditions with subsequent calculation. The conclusions for the development of a monitoring strategy and for the improvement of the quality of the prediction are that in smog situations the normalisation of the ozone content requires in the first place a decrease in the amount of non-methane hydrocarbon waste, while the level of pollution by nitrogen oxides is less important. This conclusion concerning the priority of measures to be taken to reduce the hydrocarbon waste products was reached also in other investigations. Studies in recent years have demonstrated the importance of monitoring hydrocarbons in order to develop the optimum strategy for the improvement of air quality.

A scientific strategy for the monitoring and control of air quality has been developed on this basis. The use of mathematical models combined with a monitoring system makes it possible to predict the chemical situation and to elucidate the key features in its establishment and also to formulate the necessary program of observations. In the development of measures to protect nature, mathematical models constitute a convenient instrument for reconciling economic, chemical, geophysical, and other aspects of this problem.

VIII. Conclusion

Thus mathematical modelling helps to expand the possibilities of studying the reactions of chemical compounds starting from the instant of their entry into the atmosphere to their removal from the atmosphere. Further progress in atmospheric chemistry can be achieved provided that programs for experimental measurements of the chemical composition of the atmosphere and of the rates of chemical reactions are improved and also provided that combined chemical and hydrothermodynamic models are developed in order to investigate the turnover of substances and the interaction of chemical and geophysical processes in the atmosphere. The joint consideration of atmospheric processes together with the dynamics of chemical reactions makes it possible to specify the phenomena which are responsible for the reactions of chemical substances under the influence of natural and anthropogenic factors.

Numerical modelling is used widely as an instrument for the study and development of a strategy for the monitoring of pollution and for the improvement of the quality of air in order to prevent negative ecological consequences. Since this problem has many aspects and is interdisciplinary in character, a promising approach to its solution involves the creation of expert systems for the control of the quality of the natural environment based on logical mathematical models of physicochemical and climatic processes coupled with an ecological monitoring system.

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Emission of toxic metals into the atmosphere and their accumulation in the surface layer of the Earth

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ABSTRACT. Natural emissions of metals and certain metalloids into the atmosphere are compared with anthropogenic emissions. The physico-chemical properties of metal-containing aerosols are discussed from the standpoint of the danger of environmental pollution and the distances to which these metals get dispersed in the atmosphere. The results of pollution of objects in the environment with metals on local, regional, and global levels are analysed. An assessment is made of the likely future pollution of the soil with metals.

The bibliography includes 221 references.

Contents

I. Introduction 1037
II. Comparison of natural and anthropogenic sources of metals and some metalloids emitted into the atmosphere 1037
III. Physicochemical properties of aerosols 1040
IV. Spatial distribution of concentrations of metals and some metalloids of anthropogenic origin in natural environment 1043
V. Conclusion 1045

I. Introduction

Polution of the environment by toxic metals and their compounds is a problem with several specific features. It is common knowledge that metals and other elements are subject to natural processes of migration and circulation. They systematically enter the atmosphere from terrestrial and ocean surfaces and from the space. They are also emitted by volcanic eruptions, forest fires, and other natural phenomena. Metals enter the atmosphere and disperse in it; then, after being washed out and precipitated, they are once again deposited on land and ocean surfaces. Human activity leads to additional amounts of these metals—some of them toxic—being extracted from the interior of the Earth and transported into the biosphere. As a result in certain instances environmental pollution may reach levels that are dangerous not only to the biota but also to humans. There is also an increased flow of toxic metals into layers of the biosphere supporting life and an interference with natural circulation of these metals. The picture of pollution of the biosphere and individual ecosystems is complicated by the fact that several metals and trace elements are necessary for the life-supporting processes in the biota. There are many geochemical regions on the Earth where biological objects experience a shortage of certain elements, including metals. Here the introduction of additional amounts of these elements has a beneficial effect on the biota, not a detrimental one. To assess the danger of introducing extra amounts of metals into the environment we shall use the concept of maximum permissible concentration (MPC) in each individual case. For soil we shall also make comparisons with natural background pollution.

We shall make a distinction between local pollution around the source of emission (to a distance of several kilometres, or several tens of kilometres, regional pollution (to a distance of several hundred or thousand kilometres), and global pollution (on a hemispherical or global scale). The high levels of environmental pollution in specific localities and areas where metals are processed or mined are very worrying, of course. But human activities today are conducted on such a large scale that it is the danger of global environmental pollution that has become the acute problem. Metal pollution of the environment on a global scale does not have, as yet, such tangible negative consequences as the rise in atmospheric concentrations of CO_2 or freon. But one should take into account the dynamics of global changes in metal content.

In this review we shall concentrate on pollution of the environment with such metals as Pb, Cd, As, Hg. Nature preservation experts believe that these metals should be the first to be studied.[1,2] We shall also discuss several toxic elements presenting first- and second-degree danger (Se, Cu, Co, Ni, Cr, Sb).[3] In individual cases we shall discuss, for comparison, data on certain trace elements.

II. Comparison of natural and anthropogenic sources of metals and some metalloids emitted into the atmosphere

Under natural conditions metals and metalloids are introduced into the atmosphere in the form of aerosols and vapours. These originate from dust swept up by the wind from the surface of the soil (wind erosion), from volcanic eruptions, forest fires, and cosmic dust. They also originate from the transfer of these elements through the ocean surface, from the flow of submicrometer particles and cold emission from vegetative cover, and from evaporation from the Earth's surface. It is customary to estimate the natural input of metals in the form of aerosols into the atmosphere by the product of the total amount of dust from a specific source and its elemental content. This product is expressed as mass fraction. The averaged composition of aerosols of various origins is given in the literature.[4–6] Data on the amount of dust annually emitted by natural sources into the atmosphere has wide variations: according to some it is 150–1500 million tonnes,[6] according to others it is 740–3400 million tonnes.[4] On the average wind erosion produces annually 500 million tonnes of dust (according to various authors from 200 to 1000);[4,7] volcanic eruptions produce 150 (10–200) million tonnes; forest fires 130 (20–50) million tonnes; the ocean 1000 million tonnes;[4] and vegetation from 75 to 1000 million tonnes.[7] It has been suggested that because of the rapid removal of sea salt from the

atmosphere only 10% of the amount emitted into the atmosphere is carried to the continents.[8,9] The estimates for cosmic dust are highly contradictory. On the one hand, even according to highest estimates, only the inflow of 'cosmic' nickel is comparable to the amount of this element brought into the atmosphere by soil dust.[4] On the other hand, some consider that it has been precisely the inflow of cosmic dust that has built up the trace element composition of the aerosols, the soil, the ocean, and the vegetation over many thousands of years.[10,11] In that case it is not meteoric matter but comet matter that would be the main source. This hypothesis raises some doubts because the concentrations of elements in the atmosphere over continents, over the ocean, and in polar regions differ widely. The emission of aerosols into the atmosphere by vegetation has been experimentally confirmed.[12–14] The fluxes of various elements from this source are as follows: Pb, 1.6; Cu, 2.5; Ni, 0.8–1.6; Cd, 0.2; As, 0.26; Se, 0.14; V, 0.2 thousand tonnes per year.[7,15,16] It is difficult to estimate the elemental composition of the emissions from the composition of the source itself because of fractionation. Thus, the amount of trace elements (Ag, Cu, Zn, As, Sb, etc.), compared to the amount of Fe, is considerably higher in the dust-forming soil particles than their average content in the surface layer of the soil.[17] Similar fractionation at the atmosphere–ocean[18–20] interface is due to the different degrees of enrichment (10–20 fold) of the ocean surface film with various elements. This is also due to different concentrations of these elements in the walls of bubbles formed in a rough sea.[8,21,22] Because of the high temperatures that develop in forest fires and volcanic eruptions it is mainly volatile elements that are emitted into the atmosphere.[4,8] Direct measurements of local concentrations of elements in the smoke produced by forest fires and in volcanic ashes show that these concentrations may differ by an order of magnitude or even more.[5,7]

A number of metals and metalloids may enter the atmosphere in gaseous phase. Thus, from 0.04[21] or 0.09[4] to 0.16 thousand tonnes of aerosol mercury is emitted into the atmosphere annually.[25] The source of gaseous selenium in the atmosphere are selenium-containing organic substances.[26–28] The gaseous fraction of elements (in relation to the total amount of each element) emitted in volcanic eruptions) is large: for Hg it is 64–78%; for Cd 25–40%; for Zn 22–36%; for Pb 4–7%; for As 33–49%; and for Sb 74–85%.[8]

The above data indicate that there is no single way of estimating the natural inflow of metals into the atmosphere. Of the values given by different authors only those for the trace elements brought into the atmosphere with soil dust are more or less in agreement. The greatest differences are in values obtained for elements introduced into the atmosphere in aerosol or vapour form; also for elements emitted in volcanic eruptions or forest fires.[5,7]

The most convenient way to estimate anthropogenic emissions of metals and metalloids into the atmosphere is by the amount of each element emitted per unit of it produced or per unit of fuel burnt (Table 1). Another method is used for aerosol emissions: it is based on the average concentration of metals in the dust of large cities all over the world and the global emission of industrial dust into the atmosphere. The anthropogenic emission of aerosols into the atmosphere obtained in this way is the product of these values.[4,6] The wide scatter of values for global anthropogenic emissions is due to several factors: different estimates of the total amount of emitted industrial dust and of the concentration of metals in it; different production technologies and different levels of waste purification; the difficulty of estimating emissions in vapour phase; the fact that the account emitted depends on the temperature of the source and volatility of the element.[4,5] Below we give a few examples of uncertainty in the initial data used for calculations. According to

Table 1. Emission of toxic metals per unit of production.[5,12,25,29,30]

Source of emissions	Units	As	Cd	Cr	Ni	Pb	Sb	V	Zn	Cu
Thermal power										
burning of coal	mg MWh^{-1}	42–170	18–54	310–1200	340–1470	240–2600	33–140	210–1000	216–1280	220–1000
burning of liquid fuel		87	44	155	3700	450		13 300	325	620
Industrial combustion of fuel										
coal	g $tonne^{-1}$	0.3–1.3	0.1–0.7	1.7–12	2.2–14.5	0.5–7.2	0.2–1.4	1.2–9.7	1.7–11.4	1.4–9.8
liquid fuel	g $klitre^{-1}$	1.2	0.4	7	52	6.4*		187	4.5	8.8
Refuse incineration	g $tonne^{-1}$	0.52	2.1	1.1	0.33	18–50	4.55	25	260	3.7
Burning of wood	g $tonne^{-1}$	0.3–0.5	0.2–0.3		3.1–4.7	4.7–7.0			39–58	12–19
Nonferrous metallurgy	kg $tonne^{-1}$	0.4–3.0	0.2–1.3			0.3–6.4				
Primary metal production	kg $tonne^{-1}$									
zinc, cadmium		0.6	0.1–0.5			1.2–25			15.7–17.6	0.14
copper, nickel		1–3	0.2–1.3		9	2.3–3.6	0.1		0.84–0.97	1.7–3.6
lead		0.18	0.002–0.005		0.09	3–7.7			0.11	0.06–0.07
Production from scrap metal	g $tonne^{-1}$									
copper			4.0			54–214	3		500–1630	150
zinc									9000	
lead			2.5			770			300	
Ferrous metallurgy		6–8	0.08–0.4	4–40	1.3–10	38–60			20–155	0.5–4.5
Mining of metal ores	g $tonne^{-1}$	0.1	0.5		9000	910			0.1**	100

*The emission of lead from the combustion of petrol containing tetraethyl lead is 0.37 g $litre^{-1}$.[25]

**Calculated per gramme of mined Zn + Cu + Pb.

Ostromogilskii et al.[4] the total emission of industrial dust is 80 million tonnes per year, whereas according to Izrael' et al.[6] it is between 60 and 600 million tonnes. Besides, the elemental composition of the ore or fuel (even the same type of ore or fuel) depends to a great degree on where it has been minded.[31] There is no reliable estimate of the fraction of the metals contained in raw materials and fuel that is emitted into the atmosphere as a result of industrial processes. According to Ostromogilskii et al.[4] when coal is burnt, about 10% of the Al, Co, Fe, Mn, and Sc that it contains is emitted into the atmosphere. For Cr, Cu, Ni, and V the amount is about 30%; for As, Br, Hg, Sb, and Se it is close to 100%. The gas-phase component for these elements in the emissions from metallurgical works is up to 30% for Cr, Se, Br, and Cd; up to 70% for As; and up to 100% for Hg. As a rule, the largest emissions of metals into the atmosphere come from iron-and-steel works and nonferrous metal works and by plants that burn fuel.[32] The Pb emissions come mainly from motor transport.[5]

Table 2 gives generalized data on the emission of metals and metalloids into the atmosphere from natural and anthropogenic sources. Our expert estimates of the emissions of elements into the

Table 2. Emission of elements from natural and anthropogenic sources into the atmosphere.

Element	Main sources of emission		Natural emissions,*1 1000 t year^{-1}	Anthropogenic emissions,*1 1000 t year^{-1}	Mobilization coefficient*2	Refs.
	natural	anthropogenic				
Ag	Wind erosion, forest fires	Nonferrous metallurgy	0.11 0.06—0.15	3.1 2.2—5.0	28	[4, 21, 33]
Al	Wind erosion	Nonferrous and ferrous metallurgy	$48 \cdot 10^3$	$9.1 \cdot 10^3$	0.19	[4]
As	Volcanos, wind erosion	Nonferrous metallurgy fuel combustion	8 (21)*3 3—13	40 25—80	5 (~2)*3	[4, 7, 8, 12, 21, 25, 34]
Cd	Forest fires, volcanos	Nonferrous and ferrous metallurgy, fuel combustion	1.0 0.3—7.0	7.7 5.5—11.0	7.7	[4, 7, 21, 25]
Co	Wind erosion	Fuel combustion	7.0 5.4—13	4.0 2.7—5.0	0.72	[4, 7, 8, 21, 32, 35]
Cr	Ditto	Ferrochromium production, fuel combustion	60 44—130	50 21—94	0.83	[4, 7, 8, 21, 32, 35]
Cu	Wind erosion, volcanos (ocean)	Nonferrous metallurgy, fuel combustion, ferrous metallurgy	20*4 18—22 (130)	140 56—260	7.0	[4, 7, 8, 21, 30, 35, 36]
Fe	Wind erosion, volcanos	Ferrous metallurgy	$36 \cdot 10^3$ $(30—43) \cdot 10^3$	$7.4 \cdot 10^3$ —	0.2	[4, 8]
Hg	Evaporation from continents and the ocean, wind erosion	Processes that use mercury	20*3 2.5—150	6.0 1.7—11.0	0.3	[4, 8, 11, 21, 24, 25, 32]
Mn	Wind erosion	Ferrous metallurgy, fuel combustion	600 516—750	215 107—320	0.36	[4, 7, 8, 21]
Ni	Wind erosion, cosmic dust	Fuel combustion, nonferrous and ferrous metallurgy	27 8.5—54	80 43—98	3.0	[4, 7, 15, 21, 30, 35, 36]
Pb	Wind erosion, volcanos, forest fires	Motor transport, nonferrous and ferrous metallurgy	27 4—45	425 300—470	16	[4, 7, 21, 33, 37]
Sb	Wind erosion	Fuel combustion, nonferrous metallurgy	1 0.5—1.8	24 18—38	34	[4, 8, 21, 33, 35, 36]
Se	Destruction of organic matter in the ocean, volcanos	Fuel combustion, manufacture of glass	0.6 (10)*5 0.4—3.0 (6—14)*5	7 1.1—11.7	11.7 (0.7)*5	[4, 7, 21, 25, 27, 35, 36, 38]
V	Wind erosion, volcanos	Fuel combustion, ferrous metallurgy	65 40—79	170 110—210	2.6	[4, 7, 35, 36]
Zn	Forest fires, wind erosion, vegetation	Nonferrous and ferrous metallurgy, fuel combustion	90 36—200	500 315—840	5.5	[4, 7, 8, 21, 33, 35, 36]

*1 The upper numbers give our estimate, the lower ones—the scatter of values obtained by other authors.

*2 The ratio of anthropogenic emissions to natural emissions.

*3 The values in parentheses take the gas fraction into account.

*4 The maximum estimate of the large emission of the element from the ocean into the atmosphere.[8] According to Ref. 22 this emission was even larger (170×10^8 t year^{-1}).

*5 The estimates in parentheses take into account the destruction of organic matter, especially in the oceans.[25] According to a similar estimate,[35] it is 48×10^3 t year^{-1}.

atmosphere that are listed in Table 1 were obtained by taking account of the density of distribution of values quoted by different authors.

These data apply to 1979–1980. Data are available in the literature on the emission of metals in certain European countries[7,29] and in certain regions of the USSR.[39] It should be noted that 77–87% of Pb, Cd, Hg, and As emissions occur at the latitude of 30°–70° north.[25,33,37]

Metals and metalloids with a mobilization coefficient over 1.0 can be arranged in the following sequence:

$$Sb > Ag > Pb > Se > Cd > Cu > Zn > As > Ni > V.$$

Metals with a mobilization coefficient under 1.0 can be arranged in the following sequence:

$$Fe, Al < Hg < Mn < Co < Cr.$$

There may, of course, be a much greater contribution of anthropogenic emissions on a regional and local level.

III. Physicochemical properties of aerosols

To get a correct picture of the scale and the pattern of distribution in the environment of metals and other elements that are emitted into the atmosphere and of the danger they pose to man and the biota we need data on a whole range of physicochemical properties of aerosols that contain these elements.

Vapour and aerosol-phases

Conventional air filters for aerosols (Petryanov filters, for instance) usually do not trap gaseous and fine submicrometer particles. Therefore if activated carbon[40] or a freezer set to −50 to −60 °C[41–43] is mounted behind the filter, it is possible to assess the fraction of metals and trace elements present in the atmosphere in the form of vapour or finely dispersed aerosols. Mercury has the highest fraction, from 70 to 99% of the total content.[44–46] This fraction increases as air temperature rises and decreases with growing dust content. In Japan seasonal changes have been noted in the concentration of mercury: the total concentration of mercury in the air and the fraction of it in the gas phase and in submicrometer particles is lower in winter than in summer.[47] Of the eighteen trace elements discussed in the literature,[40–42,48] Fe, Sc, Mn, V, Ba, occur mainly in the aerosol phase (over 70%). The fraction of As, Se, Br, Ag, Cd in the gas phase and submicrometer particles often exceeds 50% of their total content. The same is true for lead emitted by car engines, though its fraction fluctuates widely.[49] The aerosol fraction of Co, Cu, Zn, and Sb is low in some cases and very high in others. In the air of industrial towns the contribution of the aerosol fraction seems to be greater. Thus, in Frankfurt the aerosol fraction of Fe, Cd, Pb, Mn, and Cu is not less than 90%.[50] In the cities of the USA 96–98% of As occurs in the form of aerosols.[51] Near the ocean this value drops to 93.5%.

Density of aerosol particles

In most calculations and measurements the density of particles that contain metals and trace elements, is usually taken to be constant and equal to 1–2 g cm^{-3}. But in reality it does depend on the size of the particles. According to Watson et al.,[52] finely dispersed aerosols have a density of 1.7 g cm^{-3}, whereas that of coarsely dispersed aerosols is 2.6 g cm^{-3}. In a detailed study[53] it was noted that the density of the particles had a tendency to increase as they grew in size. Thus, if the particles are subdivided according to size into different ranges and the relationship between Fe, Mn, Zn and Cu content in the aerosol and the particle density is plotted for each range, in the range with larger particles the distribution maximum will shift to the region of denser particles. In that case the maximum will become broader. In some cases there may be two distribution maxima. Thus, one maximum for Fe, Mn, Zn and Cu occurs at a density of 2.5–2.7 g cm^{-3}, while another occurs at a density over 3.3 g cm^{-3}. As a rule the denser particles originate from the soil and consist mainly of oxides (the density of SiO_2 is 2.7 g cm^{-3}). Anthropogenic aerosols have a lower density, but they can coagulate with soil dust.

Similar results were obtained for the three-dimensional relationships between the Pb, Cd, Zn, Fe, Hg, Br, As, Cr, Co, and Mn content in road dust and the size and density of the particles of magnetic and non-magnetic aerosols.[54] Moreover, in some cases it was possible to determine the origin of the elements from the density and size of the particles (exhaust fumes, tyre rubber evaporation, soil dust, etc.). The major part of road dust consists of particles with a density of 2.2–2.9 g cm^{-3}.

Solubility of the aerosol

The fraction of water-soluble metal and metalloid compounds in the aerosol grows as the particle size decreases.[21,25] Thus, in rural areas the fraction of the soluble compounds of Cd, Pb, Mn and Zn in the aerosols for particles with a diameter $d \approx 0.1$ to 0.3 μm was 90%, and for $d \approx 5$ to 10 μm it was 80, 25, 75, and 55% respectively.

As a result, the fraction of water-soluble metal compounds in the precipitation grows with the distance from the source of emission.[56,57] In many cases this growth can be approximated by an exponential relationship. It has been found that the fractions of soluble Pb, Cd, and Cu compounds in the snow cover around a steel plant (USSR) increase linearly up to a distance of 30–40 km.[59] An increase in the fraction of soluble compounds was observed for 21 elements. However, there are isolated cases where the relationships between distance and the fraction of soluble forms is more complex; in a few cases this fraction may even decrease.[60]

The fraction of soluble Pb, Fe, Mn, and Zn compounds in aerosols over urban areas (19, 4, 33, 69%, respectively) is considerably lower than in aerosols over the ocean (84, 53, 74, 79%, respectively).[50] It has been also noted that the fraction of acid-soluble forms of metals and trace elements in aerosols tends to be smaller over continents than over oceans.[61] In rural and 'clean background' areas the fraction of soluble forms of the elements in the snow cover was (%): Pb, 21; Zn, 65–100; Cd, 65; Cu, 40–80; Co, 60; Cr, 80–85; Ni, 80; Sb, 60–70; Se, 80–100; V, 60%.[32,62] In contrast to this, near motorways the main fraction of Pb, Mn, and Ti is in a nonsoluble form.[63] In rural regions in Sweden the fraction of gaseous mercury in soluble state reaches its maximum in winter (up to 5–10%).[23]

The solubility of metal-containing compounds was found to depend on their origin. Thus, both in urban and rural areas metals and trace elements in aerosols of soil origin (e.g., Sc, La, Co, Fe) are mostly in nonsoluble form. In contrast to this, volatile trace elements of anthropogenic origin (As, Cd, Sb, Se, Cr, Cu) are found mainly in soluble form.[46] The fraction of soluble compounds is much greater in rainfalls than in dry precipitations. This is especially true for Cu (90 and 30% respectively) and Pb (83 and 5%). The fraction of soluble forms of these metals decreases with increasing pH and the concentration of insoluble Fe.[64]

Size of aerosol particles

Aerosol particles that contain metals and other elements range in size from 5×10^{-3} to 20–40 μm or more.[65] The content of dispersed elements in the aerosol is largely determined by the nature of its sources. Furthermore, it varies with the distance from the source of emission. This is due to the different residence times of particles of different sizes in the atmosphere. In aerosols emitted into the atmosphere as a result of refuse incineration 65 mass% consisted of 0.1–2 μm particles. In the emissions of iron and steel works 57% of the total amount of metals consisted of particles smaller than 2 μm.[65,66] The content of dispersed elements depends largely on the degree of purification: the better the purification, the higher the fraction of finely-dispersed aerosols that contain a large amount of volatile elements (Pb, Sb, Se, Cd, Zn, As, S).[67,68] The degree of purification has a much smaller effect on the mass fraction of such metals as Fe, Al, Ni, Mn, Co, Cu in the emissions from metallurgical works. The bulk of these metals is concentrated in particles with $d > 2$ μm.[67,69] In motorcar exhaust fumes, Pb, Br, and Cl are contained in small particles ($d < 0.5$ μm). But in the presence of large particles from road and soil dust these aerosols coagulate rapidly.[70,71] Table 3 lists the selective median (by mass) diameters of metal-containing aerosols. Two extremes are compared: the urban atmosphere and the atmosphere of the 'cleanest' and remote background areas. Aerosol particles containing most of the elements discussed earlier (except Fe, Mn, Co, Pb) have a tendency to have a smaller diameter in remote background areas than in urban or suburban regions. In the Antarctica, for instance, up to 90–95% of As, Se, Zn, Br, S, and up to 60–70% of Sc and Mn is contained in particles with $d \leqslant 0.6$ μm.[9,79] Similar estimates for the Arctic and the Antarctic are given in the literature.[66,80] However, no such relationship is observed in certain continental regions, for instance in Central Asia. This is due to the special features of the natural and anthropogenic sources in these regions.[40] According to Table 3, volatile elements (Pb, As, Cd, Zn, Cu, Se, Sb) are, as a rule, found in smaller particles than nonvolatile ones (Fe, Mn, Co, Al, etc.). This fact is corroborated by other evidence, not listed in the table: the median diameters of particles that contain Fe and Al are in the range of 2.5–7.0 μm, whereas particles containing Pb, Se, Cd, V, Zn, and Sn are characterised by $d < 1$ μm.[67]

As particles become larger, there is also a tendency for the mass fraction of nonvolatile metals in aerosols (for instance, in aerosols of soil origin) to increase. The reverse is true of volatile elements (and high-temperature sources).[71,75,78,81] The distribution of metals according to the size of aerosol particles is governed by the logarithmic normal law.[74,82] One can get not only unimodal distributions, but bimodal and trimodal distributions as well.[71,83,84]

Thus, 0.25 μm and 3 μm modes have been established for Se,[85] 0.5 and 2.5 μm modes for Pb and Br,[86] and 0.8 and 4 μm modes for Hg,[47] and so on. In many cases each distribution mode can be related to the presence of an aerosol of certain origin.[14,86] Thus, the mode in the coarsely dispersed part of the distribution is believed to be connected with soil dust.[14] The size of the aerosol particles (the metal carriers) has a different seasonal dependence in different cities.[74] It depends on precipitation[43] and on the direction of the wind with respect to the aerosol source.[70,87] In remote background areas (e.g. in polar regions) the size of the aerosol particles changes as different air masses arrive.[88,89] As a rule, with increasing altitude the aerosol particles become smaller.[81]

Enrichment of aerosols with metals

The enrichment factor

$$K_{en} = (X_i/q)_{atm}(X_i/q)_s,$$

is often used to estimate the degree of fractionation of metals and

Table 3. The size of aerosol particles that contain metals and metalloids.

Region	Mass median diameter,* mm											Refs.
	Pb	Cd	Cu	Fe	Mn	Zn	Ni	Co	As	Se	Sb	
Sudbury (Canada) (emissions from a copper-smelting plant)	0.7–1.9	0.7–5.3	4.4–9.0	9.0	4.2–5.0	0.8–6.6	9			0.7–1.0		[72]
Environs of Sudbury (Canada)	0.5–0.9	0.9–1.3	1.7–4.1	4.7–7.1	2.0–4.2	0.5–0.8	5.6–9.0		0.55–1.0	0.7–1.0		[72]
Liene (Belgium)		2.0	0.6	5.1		1.7						[73]
Large American cities	0.5 (0.3–1.0)	2.5 (1.5–3.2)	1.7 (1.1–5.8)	4.7 (2.0–9.5)	1.9 (1.2–3.1)	1.4 (1.0–1.7)	1.3 (1.0–1.5)	1.5				[71, 74]
Trebanos (England)	0.7	1.2		3.3	1.6	1.0						[71]
Ankara (Turkey)				4.5		1.2		4.5	0.8	0.5	1.2	[75]
Siberian towns (USSR)		0.9	0.5	1.2	1.1	0.5		3.0	1.9		0.9	[76]
				4.4	0.8	0.5		1.5	1.4		0.6	
Remote background areas			0.45			0.6–0.7	0.6			0.4	0.5	[32]
National Olympic Park (Washington, USA)	0.9	0.3	0.4			0.3						[71]
Semi-desert, pastures (Montana, USA)				3.0	3.0	0.6		0.2	0.5	0.3	0.3	[77]
Forest area in Tennessee	0.5				3.4	0.6						[21]
The Bermudas	0.4–0.6	0.5–0.7	0.8	2–4	2–4	0.6–0.8		1.5	0.3	0.4	0.3	[71, 78]
Eniwetok Atoll (Atlantic ocean)	0.25		0.96	0.72	0.88	0.4		0.75				[21]

*The variation range for average sizes of particles in various towns is shown in parentheses.

trace elements in aerosols. X_i and q are the concentrations of the required and the reference (typical for a particular aerosol source) elements. The subscripts 'atm' and 's' refer to the atmospheric aerosol and the source respectively. Fe, Al, and Sc (their global abundance values) are usually chosen as reference elements for soil dust, and Na or Cl for oceanic dust (ocean water).[73,90,91] The values of K_{en} reported in the literature are largely based on global abundance values. In this way it is possible to achieve a certain universality which is needed for the comparison of data on a global level. K_{en} values referred to for Al and Sc are listed in the literature.[73,90] They mainly related to areas that are at some distance from industrial sources.

These data are presented in the diagram shown in Fig. 1 for the plotting of which 500 values of K_{en} for 42 elements have been used. The elements can be divided into three groups: highly enriched ($K_{en} > 25$), moderately enriched ($3.6 < K_{en} < 25$), and slightly enriched ($K_{en} < 3.6$). As a rule, the volatile elements (I, Pb, As, Cd, Se, Hg, and others) are characterised by the highest values of K_{en}. The moderately enriched group includes Cs and Na, while the slightly enriched group consists mainly of nonvolatile elements (Fe, Ni, Sc, Mn, etc.). There is a wide variation of K_{en} values. Incidently, the values of K_{en} may vary widely even when measurements are made at one and the same site.[92] As the particles become smaller, the enrichment factor, especially for volatile elements, becomes substantially larger.[77,78,93] The results of such measurements carried out in Accra (Ghana) could be fitted with an exponential function.[75] K_{en} for nonvolatile and lithogenic elements does not increase so markedly with decreasing particle size, or it may even not increase at all.[78,93]

In some cases there is a bimodal distribution of K_{en} according to particle size.[68,78] Distribution of K_{en} as a function of geographical position depends on the location of anthropogenic and natural sources of aerosols.[5,17,21,60,77] It is mainly small particles, the most highly enriched with volatile elements, that are carried to great distances.[67] Apparently that is why replacement of global abundance values by concentrations of the elements in local soils affects the value of K_{en} considerably.[77] Quite often the K_{en} values for one and the same element emitted into the atmosphere from different sources, even in the same region, differ quite widely.[94–96] In towns K_{en} values are largely determined by industrial and transport emissions. In emissions from metallurgical works and thermal power stations the order of magnitude of K_{en} for Cd, Zn, As, Pb, and Cu is 10^2-10^3, and for Fe $K_{en} \approx 1.0$.[60] In continental rural areas K_{en} is lower than over the oceans. In polar regions (especially over the Antarctic) it is higher than over the oceans; in the southern hemisphere it is higher than in the northern hemisphere.[73,97,98] However, no such relationship has been observed in other studies.[42,90,99,100] It is not clear why the evidence is so contradictory. Possibly the different values taken for K_{en} play some part in this. There are very few data as yet on K_{en} values in the troposphere and the stratosphere.[101]

Chemical compounds of metals and metalloids

The following compounds were found in the emissions and the ambient atmosphere around plants for smelting Pb, Zn, Cd, and Cu: PbS, $PbSO_4$, $PbO.PbSO_4$, ZnO, ZnS, metallic Pb, CdO, $Zn(PO_3)_2$, metallic Cd, $Cd(OH)_2$, metallic Cu, $CuSO_4$.[102–104] The aerosol matrices contained also SiO_2, S, graphite, K_2O, Na_2O, as well as compounds of major metallic constituents, Fe_2O_3, Al_2O_3, Al_2SiO_3. As a rule, the large particles contain oxides, and the small ones sulphates.[102,105] Fourteen lead compounds were detected near the highway in a rural area and in the exhaust fumes themselves.[102,106] The following gaseous tetraalkylated lead compounds were found near two petrol stations in the USA (% of total): $(CH_3)_4Pb$, 18–46; $(CH_3)_3C_2H_5Pb$, 12–31; $(CH_3)_2(C_2H_5)_2Pb$, 5 and 12; $CH_3(C_2H_5)_3Pb$, 2 and 7; $(C_2H_5)_4Pb$, 63 and 4. However, in the residential areas of large cities and in rural areas the amount of the first compound rose to 75 and 85% of total respectively, while the last three compounds were not detected at all. This implies that ethylated lead compounds degrade much faster than methylated ones.[102,107] Lead alkyls were found in the precipitations that came down in England[108] and Norway.[109] In this case tetraethyl lead is broken down in 48 hours and sometimes cannot be detected. Organometallic compounds of Pb, H, As, and Se, which are formed when these elements react with methane, were found in the atmosphere of several towns in Japan, for instance.[110] Gaseous mercury is present in the atmosphere mainly (up to 80% of total) in molecular form (Hg^0). Part of it gets oxidised and forms unidentified compounds of Hg(II). In that case the mercury is converted into soluble form.[23] Up to 30% of Hg over Europe is in the form of dimethyl mercury, whereas over the ocean only 5% is in this form.[111] The atmosphere of remote background regions contains 11–65% Hg^0, 12–25% divalent inorganic mercury, 21–34% methyl mercury, and 1–46% dimethyl mercury.[24]

The total amount of mercury in vapour state in the air over the Almadena mercury mine (in Spain) was made up of the following: Hg^0, 17–100%; methyl mercury, 0–66%; inorganic Hg(II), ~30%. There was also a small amount of dimethyl mercury.[112] As

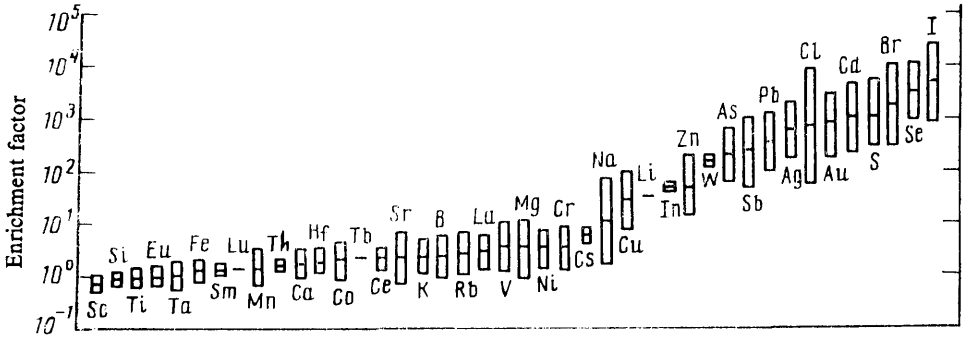


Figure 1. Enrichment factor, K_{en}, for elements in atmospheric aerosols in relation to global abundance ratio (with Al taken as the reference element).[90]

regards arsenic, in Japan up to 10% of it is found in aerosols in the form of organic compounds.[113] The organic particles consist mainly of dimethyl arsinic acid. In summer its concentration rises. Bromine compounds such as methylene bromide, methyl bromide, bromoform, and others were found in the atmosphere of Alaska, New Zealand and elsewhere.[114]

IV. Spatial distribution of concentrations of metals and some metalloids of anthropogenic origin in natural environment

The distance to which a pollutant may spread in the atmosphere largely depends on at least two factors: on how quickly it (a) disintegrates and (b) is transferred to the surface of land and ocean as 'dry' or wet precipitation. These processes have been discussed in detail in reviews,[115–118] and the respective theoretical calculation have also been performed.[119–122] The concentration of vapours of elements in atmospheric precipitations is governed by Henry's law. The Henry coefficient for Hg vapour is 0.48.[116] Dry precipitation of aerosols is connected with sedimentation due to gravity and turbulent air flow directed towards the surface of the Earth. It increases markedly with the height and density of vegetation.[119,123,124] The rate of dry precipitation falls as aerosol particles decrease in size to 1–2 μm, and then rises slightly again at $d < 0.1$ μm because of improved diffusion of very small particles towards the surface of vegetation in the boundary layer (near the Earth's surface where the wind velocity is zero).[15,119,124] The removal of the aerosol admixture from the atmosphere with precipitation is the result of two processes: capture of the aerosols by cloud drops inside the cloud (rainout) and by raindrops below the cloud (washout).[115–118] The mode of capture may vary widely: Brownian and convective diffusion, inertial capture, thermophoresis, etc.

Of the aerosols deposited by precipitation, 0.1–1 μm[116–119,124] particles have the smallest washout rate. In other size ranges the washout rate may be higher by one or several orders of magnitude. According to certain estimates, snow washes out aerosols much more effectively than rain.[117,125] The opposite applies to gases.[118] Snow flakes can capture aerosol particles of different sizes equally well and do so very effectively.[126] This contradicts the theory and needs to be confirmed. As a result, the total (dry and wet precipitation) rate of removal of aerosols from the atmosphere also falls at first as the particle size decreases approximately to 1 μm. In the 0.1–1 μm range the rate remains very small. Then for the even smaller (submicrometer) particles the rate rises once more. However, aerosol filters are unable to catch such particles effectively.[40,42,43] This should be taken into consideration when analysing the behaviour of the aerosol. Let us roughly assume that the rate of removal of aerosol particles from the atmosphere increases with particle size. There is experimental evidence that after precipitation the concentration in the air of the coarsely dispersed fraction of the aerosol drops more sharply than the concentration of the finely dispersed one.[43,127,128] In remote background areas the larger soil particles were also washed out more rapidly than the anthropogenic ones.[89]

The average residence time of atmospheric aerosol in the troposphere is believed to be 1–3 days. But when there is local precipitation of very large particles the residence time is no more than several hours. The residence time of gases in the troposphere is measured by months and years.[117,129]

Chronic exposure of metals and trace elements has the most serious effects. It is therefore important to know the mean monthly and annual concentrations of metals and trace elements in the atmosphere to allow us to assess the danger they pose. The highest concentrations, often in excess of maximum permissible concentrations (MPC), were observed in large cities and around emission sources, especially in the vicinity of metallurgical plants. Thus, in Mexico City cadmium concentrations were 10 times higher than MPC, Zn concentrations were 20 times higher, and Pb concentrations several times higher.[130] There is similar pollution in the cities of the FRG[131] and the USSR. In rural areas, in remote background terrestrial areas, over oceans and in polar regions the concentration of metals in the atmosphere is significantly lower. Thus, for Pb there is a difference of 4–5 orders of magnitude. In the centres of large cities concentrations of Pb in the air amount to $(1-10)\times10^{-6}$ g m^{-3}. In suburbs and rural areas it is lower by 1–2 orders of magnitude.[132] The average concentration of Pb in background areas is (g m^{-3}): for polar regions 0.1×10^{-9}; for 35°–65° N. lat., 10^{-9}; for 0–30° N. lat., 0.2×10^{-9}; for 0–30° S. lat., 0.3×10^{-10}; for 25°–55° S. lat., 15×10^{-10}; for Antarctica $10^{-11}-10^{-12}$.[133–135] In several cases a relationship was observed between lead concentration and the number of dwellers in the city.[136] Cadmium concentrations in the air of USA cities varies within the limits $(1-100)\times10^{-9}$ g m^{-3}. In British cities the average concentration of arsenic is 2.8×10^{-9} g m^{-3}. In rural areas in the USA it is $(4.0-0.3)\times10^{-9}$ g m^{-3}. In Antarctica it is 0.01×10^{-9} g m^{-3}.[21,135,137] The concentration of arsenic in the air of British cities is 6.4×10^{-9} g m^{-3}; at the South pole it is 6×10^{-12} g m^{-3}.[21]

It is interesting to note that the concentrations of Fe, Se, Co and of rare-earth elements, which are usually found in the larger particles, fall tens of times more rapidly with distance from the continent than the concentrations of Se, Sb, and other elements.[138] In the past decade a distinct tendency to lower the air pollution levels of Pb, Zn, Cu, Cd, V, and Mn has become evident in a number of foreign cities and remote background areas.[134,139–143]

There is much less difference between the concentrations of mercury, which is mostly present in vapour state. Thus, the Hg concentrations in USA cities is between 5 and 50 ng m^{-3}; in rural areas it varies from 3 to 9 ng m^{-3}; and over the waters of the Pacific and the Atlantic oceans it is 1–3 ng m^{-3}; in the Southern hemisphere it is only half that in the Northern hemisphere.[23,144] Around certain natural sources the Hg content may amount to 10^3 ng m^{-3}.[145] The vertical distribution of metals in the troposphere is complicated, with a general tendency for the concentration to decrease with height. There is an alternation of maxima, which reflects the fact that there are temperature inversions, advections of various air masses, and other factors.[101,146–148]

In Swiss cities in summer time the distribution of Cd, Cu, Mn, Pb, and Zn concentrations at 515–1500 m above sea level was found to be homogeneous.[149] In the USSR the maximum concentration of Hg in the lower troposphere was observed over the Urals.[150] There are very few experimental data on the amount of organic compounds of metals in the air and the precipitations. The concentration of tetraalkyl lead in European and American cities in 1978–1981 was 83 ng m^{-3}; on roads and in traffic tunnels it was up to 100–200 ng m^{-3}; in housing estates it was 20 ng m^{-3}; and in rural areas 1.7 ng m^{-3}.[151] In Norwegian cities it varied from 11 to 81 ng m^{-3}.[109] Earlier publications gave the concentration of tetraalkyl lead in city air as several micrograms per m^3.[49,132] Let us remember that MPC for a single exposure to tetraalkyl lead in a working zone is 75 g m^{-3}.[152] Most of the arsenic in atmospheric

precipitations is in the form of inorganic compounds.[153] The average concentrations of arsenites and arsenates in the region of the Hawaiian Islands were 0.007 and 0.012 parts per billion respectively; in the area around the Tacoma, WA, USA smelting works they were 1.06 parts per billion.

Soil and snow cover become polluted with metals brought from the atmosphere with 'dry' and wet precipitations. The spatial distribution of metals in these media around the source of emission follows the same pattern as in the surface layer of the Earth. The greatest danger of pollution is within the 10–20 km radius around the emission sources[154,155] and further.[68,72] The boundary of the polluted soil area is very arbitrary, because it is difficult to separate the natural (background) metal-content in the soil from the amount of metals derived from anthropogenic sources. The average levels of pollution of natural media by a local source are inversely proportional to the square of the height of the emission.[156] But the higher the emission takes place, the larger the amount of metals carried to great distances (regional and global pollution). The configuration of the local zone and the degree of its pollution also depend on the wind rose, the vigour and duration of the emissions, the particle size composition, and the frequency of precipitations when wind direction varies.[157,158] What is precipitated locally consists mainly of coarse particles (according to Izrael' et al.[6] global precipitations consist of particles with $d < 5$ μm). The relationship between the level of pollution of natural environment with metals and the distance from the source of emission is thought to follow approximately an exponential dependence in some cases, and a power dependence in others,[159,160–162] with the exponent close to -1.[72,163–166] The parameters of both the exponential and the power distributions are essentially determined by the velocity of the wind, how often it blows in a particular direction, by the height and vigour of the emissions, as well as by other factors. It is difficult to decide which of the above functions gives a more objective picture of the real situation. However, the theoretical dependence of aerosol concentration on the distance from the source becomes, after passing the maximum, close to a power dependence.[118] More complicated models of local precipitations, based on the theory of aerosol distribution in the atmosphere, are discussed in the literature.[119,167,168] From 10 to 40% of the respective emissions of Pb, Zn, Cu into the atmosphere were found to be precipitated in the local zone around a number of metallurgical works in the USSR.[169] By other estimates local precipitation of several metals around iron-and-steel works amounted to 15–37% of the emission of the respective element; around thermal power stations it amounted to 40–50% of the emission of the respective elements.[159]

Measurements taken in the region of the Sudbury copper works (in Canada)[69,72] showed that in a 40 km radius the following amounts of metals were precipitated from emissions from two chimneys 194 and 381 m high in the absence of natural precipitations: Fe, 15.2; Al, 8.9; Ni, 2.6%; finer aerosols Pb, Zn, and Cd, less than 2%. On days when there were natural precipitations the figures were: Fe, 68; Cu, 100; Ni, 36; Zn, 92; Al, 80; Cr, 14.2; Cd, 9.7%. On dry days the fraction of precipitations in the above zone for emissions from a chimney 93 m high was: Fe, 100; Ni, 29; Al, 58; Pb, 13; Cd, 1%. For Hg the respective indices were considerably lower: for operating chlorine-alkali plants the fraction of local mercury precipitations in a 10 km radius was from ~7%[170] to 10%;[23] in a 3 km radius it was 5%.[171]

It has been postulated that Hg can go through repeated precipitation and evaporation cycles,[46] finally accumulating in the polar regions in low-temperature conditions. But so far there has been no direct confirmation of this hypothesis.

Local zones with soil highly polluted with metals are often regarded as technogenic geochemical anomalies.[172,173] These zones are doubly dangerous because in such zones the fraction of metals in mobile and exchangeable state, and, consequently, easily assimilated by plants, is often significantly higher than in remote background areas.[154,165,174,175] In the zone of local precipitation the aerobic assimilation of metals by plants through their leaves and stalks plays a prominent role. This effect decreases with distance from the source of emission.[176,177] The combined effect of the extremely toxic compounds of sulphur and nitrogen with metals causes plant diseases and the destruction of forests and other vegatation, and reduces crop yields.[178–180]

Regional precipitations, and the more so global precipitations, usually do not lead to a significant increase of the amount of metals in the soil. However, it was established that in Norway the soil contained different amounts of lead: from 100 to 120 p.p.m. in the south to background levels of 10 p.p.m. in the north. This difference may be due to lead emission in Western Europe.[181] Areas of snow cover considerably polluted with metals extend over 10 to 13 thousand km^2 around Norilsk and Monchegorsk.[182]

Because car exhaust fumes are emitted close to the ground, soil and snow become polluted with lead and other metals in areas adjoining the highways to distances not greater than some tens and hundreds of metres.[86] Only 0.2–0.7% of Pb and 1.7–5.5% of Zn in this zone are in an exchangeable state.[183]

Technogenic toxic metals enter the oceans mainly from the atmosphere. Nearer the continental shelf river discharges start to play a greater role and both these factors become commensurate.[21] The maximum concentration of Pb in the surface layers of the Pacific ocean (up to 14–16 ng m^{-3}) is observed at mid-latitudes (20°–40° north lat.). Lead concentration is lower in the tropical zone (down to 6 ng m^{-3}), and in the southern hemisphere it is only 4–5 ng m^{-3}.[184,185] The natural level of lead in the surface layers of the northern Atlantic and Pacific oceans is exceeded by a factor of 8 to 20 and in the southern part of the Pacific ocean it is exceeded by a factor of 2. The vertical profile of Pb concentration has its maximum in the layer 0–2.5 km in depth. In deeper layers the concentration drops 6- to 7-fold.[21,184,185] The Cd, Zn, Cu, and Ni content in the ocean grows with depth down to 1000–1500 m, and in individual cases even to greater depths.[21,187] It is difficult to speak of the fraction of anthropogenic metals in this case. We can assume that deep in the oceans the concentrations are still at preindustrial levels, because vertical exchange takes a very long time.

It is interesting to trace how the anthropogenic emission of metals into the atmosphere increases the pollution of the environment on a global level on the example of polar regions, where biota is most sensitive to outside influences. In winter, when the polar front moves far down south, large masses of pollutants move into the arctic regions to form an aerosol haze there.[188–191] This haze contains sulphur and nitrogen compounds, polycyclic aromatic hydrocarbons, organic compounds, and soot, as well as metals and metalloids.[137,192–195] In winter, because precipitations are few and there is stagnation in the atmosphere, the lifespan of fine aerosol in these regions can last up to 2–3 weeks.[46] Plotting circulation paths in conjunction with the use of reference materials, together with other methods allows us to conclude that the polluted air masses move into the Arctic from Europe and to some extent from North America. Most of these masses settle in the European part of the USSR and in the Urals.[196,197] No similar phenomena have been

observed in the Antarctic. In spite of the presence of an anthropogenic polar 'haze', measurements of Hg, Cd, Zn, As, Cu, Sb, and Se concentrations in different layers of a glacier in Greenland gave no reliable proof of an increase in these concentrations in the industrial period.[133,198,199] This may be due to methodological difficulties (external pollution of the samples)[133,134] and to the wide scatter of data. It has been found that even in the pre-industrial period the concentrations of metals in the atmosphere were much higher during glaciation than in the interglacial ages.[134,200] The metals must have been of soil origin because the data correlate with Al. Pb is the exception: its content in the ice of Greenland in the period from 800 to 1950 AC increased 200 times (from 1.4×10^{-12} to 200×10^{-12}).[201] According to other evidence, by 1965 the content of Pb amounted to 230×10^{-12}; then by 1983 it decreased several times because a number of countries had prohibited the use of ethylated petrol.[134] In the Antarctic also no rise was observed in the concentrations of metals and metalloids (Hg, Cd, As, Fe, Zn etc.) in layers of ice dating from the industrial period.[133,199,202–204] Here too Pb was the only exception. However, estimates of the rise in its concentration in the industrial period are somewhat contradictory. In the ice of Antarctica lead concentrations increased 4- to 5-fold.[202–205]

There is also a different estimate.[133] According to it, the concentration of Pb in the ice layer increased to a somewhat lesser degree: from $(1-2)\times10^{-12}$ to $(2-5)\times10^{-12}$. Attempts were made[134] to assess the concentration of lead in the air of Antarctica in the preindustrial period on the basis of the current contents of lead in the glacier and in the atmosphere (7×10^{-12} and 1×10^{-12} g m^{-3}, respectively).

It is difficult to estimate the danger of regional and global pollution of the atmosphere with metals because there are no standards as yet. Such pollutions are relatively low-level, but they spread over large areas. Local pollutions are estimated by comparison with MPC, but this method has significant drawbacks. Every MPC refers to a specific metal or substance,[152,206,207] whereas in natural conditions there is a mixture of toxic substances. Some of them have a joint synergic effect on the Biota, whereas others have an antagonistic effect. Attempts to develop some standards for pollution of the environment by mixtures of toxic substances remain purely formal so far.[208] The concept of 'maximum permissible load' on the ecosystem has been proposed, but so far it has found no practical application.[209] It is still not clear what units should be used to measure this load. We believe that biomarkers characterizing the reaction of biological objects to pollution should be used to assess the danger of pollution of the environment by a combination of toxicants.[210] Suggestions have been made concerning the assessment of soil and air pollution with metals.[158,211,212] The concept of the maximum permissible emission (MPE) is widely used to safeguard against dangerous pollution levels. MPE is the emission after which the atmospheric concentration of a toxic substance does not exceed its MPC.[213] This concept has also been applied to the content of toxic metals in the soils around metallurgical works.[214] In general, it is necessary to set up such MPE values which would guarantee that the MPCs would not be exceeded in all natural environments. A serious drawback of MPCs for the atmosphere consists in these standards being determined with no regard for the dispersion properties of the aerosols, whereas it is mainly the finely dispersed aerosols that settle in the respiratory tract and the lungs. Most of Pb, Cd, Cu, Zn, Mn, and Fe from the atmospheric aerosols settle in the lungs (10–40% of the inhaled amount). If we consider the whole respiratory tract, including the nasopharynx, 50–90% of Fe, 30–42% of Pb, 40–70% of Cd, 28–62% of Zn inhaled are deposited there.[71]

V. Conclusion

Today there is a high level of air and soil pollution because of the emissions of metals into the atmosphere. In many cases the pollution exceeds the MPC. This is mainly true for large cities and centres of industry, especially if they contain nonferrous metal works or iron-and-steel works. Excessive amounts of toxic metals in the environment, especially if there are other toxicants as well, lead to diseases in man (including cancer). They also promote diseases of arboraceous vegetation and its destruction, and they reduce crops.[177,179,215–217]

A further rise in the pollution level is to be expected in the foreseeable future. This applies especially to soil, the surface layers of the oceans and the polar regions. It will be caused by a greater volume of emissions and by the accumulation of precipitations. Thus, the average annual global increase of emissions of metals into the atmosphere in 1950–1975 was for Pb, 3.1%; for Cd, 4%; and for Ni, 6.7%.[218] According to Ostromogil'skii et al.,[25] the worldwide emission of Pb will rise in the period 1980 to 2000 by 10%; for As and Cd this increase will amount to 20%. It takes from several months to several years to double the natural background amount of metals in a surface layer of soil 1 cm thick near a metallurgical plant.[165,219] In American cities it takes several tens of years to double the background amount of Pb, Cd, Zn in a 2.5 cm thick surface layer of soil; in residential areas it takes a hundred years or longer.[220] In rural and remote background areas the natural concentration of most metals in the 1 cm thick surface layer of soil also doubles in tens and hundreds of years.[165]

Calculations predicting the level of pollution of the environment with Pb, Cd, As, and Hg were carried out for 1980–2000 on the basis of the 'box' model.[25] One can expect the concentrations of Pb, Cd, and As in the air of nonindustrial terrestrial regions in the northern hemisphere to grow by several percent (up to 10%). In Antarctica they can be expected to grow by 25, 15, and 10% respectively. The Pb concentration in the surface layer of the northern part of the Atlantic ocean will almost double by 2010. In other parts of the ocean it will rise by tens of percent.

The maximal level of pollution of soil and ocean, which accumulate the metals emitted into the atmosphere, will be established after all the industrial reserves of these metals have been exhausted and they themselves have been dispersed over the globe. Even rough estimates[221] show that the amount of lead, mercury, cadmium, and arsenic in the soil will be tens and hundreds of times greater than at present. The migration of elements from the surface layer of soil into rivers and oceans is a very slow process. Because of that the achieved high levels of pollution of the soil with metals will be maintained for a long time (for hundreds or even thousands of years). This makes it so important to strive already today to reduce sharply the emissions of metals into the atmosphere and their dispersion in the environment by adopting progressive technologies and waste-free manufacturing processes.

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Determination of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls and chlorine-containing pesticides in the environment

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ABSTRACT. Literature material has been correlated on methods of determining ecologically particularly dangerous polychlorinated compounds (dioxins, furans and biphenyls) and chlorine-containing pesticides and phenols in the environment, viz. in air, natural waters, soil, sludges and various tissues of biological organisms (including man). All stages of the analysis are reviewed, i.e. selection and storage of samples, methods of extraction and derivatisation, means of purification of organic extracts, gas chromatographic and gas chromatography-mass spectrometry methods of separating and estimating individual isomers and compounds and their detection limits.

The bibliography contains 164 references.

Contents

I.	Introduction	1051
II.	Insecticides	1051
III.	Biphenyls	1053
IV.	Herbicides	1054
V.	Phenols	1055
VI.	Dioxins and furans	1055

I. Introduction

Polychlorinated organic compounds (dioxins, furans, biphenyls) and chlorine-containing insecticides, herbicides and phenols have currently become a global ecological hazard because of their fairly high toxicity for mammals, including man, their persistence and their universal distribution both in the environment and in foodstuffs. Particular danger is presented by the 12 isomers of dioxin and furan containing 4–6 atoms of chlorine, of which 4 must be in positions 2, 3, 7 and 8 , and 13 isomers of biphenyl containing 4–7 chlorine atoms of which 4 must be in positions 4,4′ and/or 3,3′ and 5,5′. These isomers are very toxic compounds, they are synthesised by man and reliable methods have been developed for their quantitative determination at the ppt level (ng kg^{-1}). The limits of detection of chlorine-containing pesticides and their metabolites have been reduced significantly. The metabolites proved to be either precursors of xenobiotics of the dioxin type or synergistic with them.

The review is devoted to an analysis of the work of the last 5–7 years on the methods of determining quantitatively polychlorinated compounds of the types indicated. Special attention has been allotted to the isomer-specific determination of dioxins, furans and biphenyls.

II. Insecticides

Chlorine-containing insecticides are applied in the struggle against harmful insects. In this section most attention will be paid to the determination of 4,4′-dichlorodiphenyltrichloromethylmethane (DDT), its metabolites 4,4′-dichlorodiphenyldichloromethylmethane (DDD) and 4,4′-dichlorodiphenylchloroethylene (DDE) and also of the isomers of hexachlorocyclohexane (HCCH).

1. Selection and storage of test samples

Test samples of natural waters are taken with glass, teflon or metallic samplers, from vessels or bathometers. The volume of sample taken may vary from 4–25 litres depending on the assumed concentration of insectide.[1–4] It is not subjected to conservation and storage in view of the possible loss of insecticide as a result of adsorption onto vessel walls. Consequently it is necessary to extract the samples taken with an organic solvent, frequently hexane, within 2 hours. The organic extracts are stored in bottles with ground-glass stoppers. It is best to store them in the frozen state.[3] After storage at room temperature analysis must be carried out no later than 3 months after taking the sample.[1,2]

Sludges are selected with various hollow tubular samplers to avoid mixing when taking samples. Usually 10–15 cm upper layer of sediments is taken.[4–6] They are stored in glass jars at 4 °C or at −10 to −15 °C.[4,6] At room temperature samples may be preserved by acidification with hydrochloric acid to pH 2 and stored in that form for a month.[6]

Soils are sampled with an auger or a scoop and samples are mixed. They are air-dried in the laboratory or in the open air. They are stored in the dry state in small linen bags, and if naturally moist in the refrigerator.[7]

Test samples of air are always concentrated by passing them into liquid[8] or solid[9] adsorbents. The volumes of air may therefore amount to thousands of cubic metres.[9]

Biological samples are stored in the frozen state at −10 to −78 °C.[4,5,10–16] Only freshly taken samples must be frozen.

2. Extraction

Insecticides are usually extracted from test samples of natural waters with hexane[1–3,17,18] or dichloromethane.[4] The organic extract is dried with anhydrous sodium sulphate. The solid phase extraction of insecticides with microcolumns of charcoal and Tenax[19] and also with phases used for liquid chromatography[19–21] is extremely promising. The concentration factor may reach 1000 which permits the use of small volumes of water or eluates and excludes removal of solvent prior to gas chromatographic analysis (GC).

For soils an average test sample is first taken by quartering from the air-dried mixed specimen, roots and stones removed, and the sample then ground and screened through a sieve of pore diameter 0.5 mm. The efficiency of recovering insecticides from soils depends markedly on their type and their absorptive powers. Consequently it is suggested that the the optimum means of extraction of insecticides is selected for each test sample from three parallel subsamples.[7] After keeping the dry sample in distilled water the insecticide is extracted in the first extraction method with a mixture of hexane–acetone 4:1, in the second with a mixture of acetone–hexane 1:1 in the presence of 1% ammonium chloride solution and in the third with acetone with the same salt added.[7,17]

Preliminary deactivation of soils with ammonium chloride solution and subsequent extraction of insecticides in an ultrasonic bath with acetone and further re-extraction with hexane frequently enables analysis of extracts by GC with an electron capture detector (GC/ECD) without further purification.[22] It was shown that treatment of soils with 20% BF_3 in methanol prior to extraction increased the amount of HCCH isomers extracted by up to three times compared to any other extraction method.[23]

Insecticides are extracted from sludges, after homogenisation, with acetone[6] or with dichloromethane.[4]

Insecticides are often extracted from biological material with acetone–hexane mixtures in various proportions with simultaneous homogenisation of the biosample.[11,17] Acetonitrile or acetone is usually used for plant tissues.[24] Insecticides are then quantitatively transferred from water-soluble solvents to water-insoluble solvents, usually into hexane, cyclohexane or dichloromethane for purification.

Most frequently biosamples, after homogenisation, are dried with anhydrous sodium sulphate at a ratio of 1:4, the mixture is ground to a powder[5,10,14,25,26] and the insecticides extracted with an organic solvent in a chromatographic column or in a beaker.

Insecticides are usually extracted from milk with solvents,[16] however recently it has been suggested that extraction is carried out after adsorption of milk components on special cartridges,[27] silica gel[28] or Florisil.[29]

When it is important to know the lipid content of the biosample, extracts are evaporated to dryness, the mass of lipid determined in the dry residue, which is then dissolved in organic solvent for purification.

3. Purification of organic extracts

Removal of organic substances co-extracted with insecticides which interfere with analysis is achieved by treatment of hexane extracts with concentrated sulphuric acid until a colourless layer is obtained.[1–3,6,7,17,30] This method of purifying extracts is only used when acid-stable insecticides are being determined, for example DDT and its metabolites, HCCH isomers, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB). When analysing acid-unstable insecticides extracts are purified on adsorbents in chromatographic columns.

It should be mentioned that elemental sulphur and organosulphur compounds are often present in organic extracts of soils and sludges. These are not removed by acid treatment but interfere with the determination of HCCH isomers. Sulphur compounds are removed by adding to the hexane extracts solutions of tetrabutylammonium sulphate and sodium sulphate in the presence of isopropyl alcohol[6,7] or activated metallic copper.[4]

Insecticides of low stability in acid media, and they are the overwhelming majority, are separated from the interfering organic matrix usually on chromatographic columns of Florisil, silica gel or Al_2O_3,[5,8,11,13–16,18,21,24–27,29–32] or by high performance liquid chromatography (HPLC).[33] This purification may be automated.[34] A very efficient means of separating insecticides in extracts of animal and plant tissues is exclusion (gel-permeation) chromatography,[10,11,24,26,35] one of the variants of HPLC. Styrene-divinylbenzene gels, such as BioBeads SX2 or SX3, are used for this. Only 0.02% lipid remains in extracts after this treatment.[11]

4. Separation of insecticides in extracts

Extracts of insecticides (DDT, DDE, DDD and HCCH), purified from organic substances, may be analysed in gas chromatographs with packed columns only when contamination by PCB and many acids-unstable insecticides which interfere with the analysis is absent. In the majority of samples however, such contaminants are present and consequently extracts are usually fractionated.

Extracts of insecticides purified with sulphuric acid are subjected to alkaline dehydrochlorination with alcoholic alkali. In this case hydrochloric acid is split out from molecules of DDT, DDD, and HCCH while molecules of DDE, PCB and HCB are practically unchanged.[1,2,6,7,15] It should be mentioned that on Florisil, in addition to separating intefering organics from insecticides, it is possible to separate PCB from insecticides[13] and resolve insecticides into fractions[10,11] by changing the eluting solvents.

In the majority of cases extracts of insecticides purified on Florisil are resolved into fractions on silica gel,[5,8,26,30] after which they are analysed by gas chromatography.

The simultaneous purification and fractionation of insecticide extracts on one chromatographic column of aluminium oxide and silica gel[25,31] is of practical interest. This enables time and solvent volumes to be reduced.

5. Gas chromatographic separation and detection limits

Purified fractions of insecticides are analysed by GC/ECD usually on packed columns. If PCB are present in the extracts then fractions are analysed in the chromatograph prior to and after dehydrochlorination. The limit of detection of insecticides and PCB in sea and fresh water, depending on the sample volume taken, is equal to: for DDT and its metabolites 0.03 [3] and 0.2–3.8 ng litre^{-1},[1,2] α- β-, γ- and δ-HCCH 0.01 [3] and 0.2–1.3 ng litre^{-1},[1,2] PCB 0.2–20 ng litre^{-1};[1,2] in sludges: for DDT and its metabolites 0.3–0.5 [6] and 5 ng g^{-1} (SP-2250 or SP-2401 columns),[5] lindane and heptachlor 0.,1 [6] and 5 ng g^{-1},[5] α- and γ-HCCH, aldrin etc. (13 insecticides in all) 5 ng g^{-1},[5] PCB 30 [7] and 20 ng g^{-1};[5] in fish: for DDT and its metabolites 0.6 μg g^{-1} of fish fat,[17] 21 insecticides 10 ng g^{-1},[26] 19 insecticides 2–40 ng g^{-1},[10] PCB 0.6 μg g^{-1} fish fat[17] and 100 ng g^{-1};[26] in soils: for DDT and its metabolities 2–3 ng g^{-1}, α- and γ-HCCH 0.2 and PCB 30 ng g^{-1} dry weight.[7] Retention times for 28 insecticides on 9 different packed columns have been published.[36]

Recently insecticides and PCB have also been analysed on quartz capillary columns. This enables the simultaneous determination of significantly more insecticides from only two fractions.[11,26,31] Thus it is possible to determine 19 insecticides and 7 PCB isomers in biosamples on columns of length 25 m of CP-Sil 5 CB or CP-Sil 8 CB,[31] 37 insecticides in human adipose tissue on columns of length 15 m of DB-5 or DB-17 with a limit of detection of 0.9–14.3 ng g^{-1},[11] 28 insecticides in topsoil on columns of length 25 m of OV-1701, OV-17 and SE-52 [22] and 12 insecticides in water

on a column of length 30 m of SPB-608 with a limit of detection 10 ng litre^{-1} [by GC-mass spectrometry (GC-MS)].[19]

III. Biphenyls

1. Sample treatment

The PCB are a mixture of substances used as oils for transfomers, hydraulic fluids, dielectrics, etc. In different countries PCB have their own trade names, for example trichlorobiphenyls in the USSR, Sovols in France, Arochlors in USA and Chlophens in FRG. They are in turn divided into types reflecting the percentage chlorine content in the mixture and the number of chlorine atoms in the molecule. For example, Arochlor 1254 series 1200 contains 54% chlorine, it has an average of 4.9 chlorine atoms per molecule and an average molecular weight of 324, Chlophen A-50 contains 50% chlorine, and a pentachlorobiphenyl of the type of the electrochemical Sovol has 54%.[7] These are frequently used as standards in the determination of PCB.

Since PCB are met, as a rule, in the environment together with the various chlorine-containing insecticides, all these substances are usually determined in one sample. PCB are separated from acid-stable insecticides by alkaline dehydrochlorination and chromatograms are compared prior to and after dehydrochlorination. Insecticides are determined from the difference in peaks on the two chromatograms and PCB from the total peak heights in the second chromatogram. PCB are usually separated on silica gel (see above) when determining acid-stable insecticides. The limit of detection of total PCB content in natural water is 0.2–20 ng litre^{-1},[1,2] and in sea sludges and soils 2–5 ng g^{-1} dry weight respectively.[6,7] Chlophen A-50 is used as a standard for PCB.

When determining PCB the selection, storage and treatment of samples of environmental objects is generally the same as for insecticides (section II). Mention may also be made of the concentrating of PCB from contaminated natural waters with adsorbent C_{18},[37] the purification of extracts by HPLC with subsequent determination of PCB by GC/MS,[38] loss of the overall PCB content up to 56% and of each isomer separately when drying sludges at 60 °C for 48 h,[39] and also the possibility of combining purification and determination in one sequential system LC-GC/ECD,[40] which enables determination of PCB to be automated.

Methods have been described for determining many individual PCB isomers in various biological samples, such as whales,[41] penguins and their eggs,[42] molluscs,[43] sea mammals,[44] fish,[45–50] animal tissues,[51] milk [52] and human blood.[53] It is necessary to mention that PCB isomers from bound fats (phospholipids) must be separated quantitatively by saponification with subsequent extraction with polar solvents.[39]

2. Gas chromatographic separation and determination

The quantitative determination of PCB for individual types of PCB, such as Chlopen A-50 or Arochlor 1254, is difficult since different types of PCB or mixtures may be present in the environmental samples. Consequently several individual types of PCB or mixtures have come to be used as standards in recent years. For example, Arochlors 1242, 1248, 1254 and 1260 are used as standards for the determination of PCB in soil and grass with a limit of detection of 1 ng g^{-1} dry weight.[54] The same standards are used for lake deposits but with quartz columns,[55] and a mixed standard containing equal amounts of Arochlors 1242, 1254 and 1260 is used for soil with a limit of detection of 0.5 ng g^{-1}.[56]

Cross-calibration in the determination of actual amounts of Arochlors 1242 and 1254 and their sum in contaminated residues using seven individual standards containing Arochlors 1221, 1232, 1016, 1242, 1248, 1254 and 1260 showed that the relative standard error of the GC/ECD method using packed columns was 30% and of the GC/MS method using capillary columns was 38%.[57] Occasionally internal PCB standards, such as 2,4,5-trichloro- and 2,2′,3,4,5,6-hexachlorobiphenyl are added to test samples of sludges and entrapped water with subsequent determination by GC/ECD on capillary columns with 84–99% detection of standards.[58]

In view of the importance of Arochlors as standards the percentage of isomeric groups is determined in each of them by GC/MS. For example, Arochlor 1254 has Cl_4 16.0, Cl_5 59.9, Cl_6 23.8 and Cl_7 0.4% and Arochlor 1268 has Cl_7 4.0, Cl_8 36.3, Cl_9 52.3 and Cl_{10} 7.4%,[59] and a series of Arochlors may contain up to 60 individual isomers.[60]

The inadequacy of comparing concentrations in a test sample with that of determined Arochlor or Chlophen is reinforced by the change with time of the 'PCB picture' in the environment as a result, for example, of isomerically specific disintegration, biotransformation and bioaccumulation by living organisms. Furthermore the problem of quantitatively determining PCB will be aggravated by the removal by nature of individual PCB isomers in chemical and pyrolytic processes. In addition to the reasons mentioned above the precision of determination in environmental samples will also markedly depend on the variability and sensitivity of each isomer to the method being used.

In all 209 PCB isomers are known: Cl_1 (3), Cl_2 (12), Cl_3 (24), Cl_4 (42), Cl_5 (46), Cl_6 (42), Cl_7 (24), Cl_8 (12), Cl_9 (13), Cl_{10} (1), each has been given a number from 1 to 209.[60–62]

For more precise determination of PCB in samples the use of calibration mixtures of PCB isomers at various concentrations has been proposed. These include one isomer from each isomeric group, with a number of chlorine atoms from 1 to 10, and analysis by GC/MS.[63] Identification and quantitative determination of PCB isomers by the actual number of chlorine atoms is effected by their detection in a particular mass range in the mass spectrogram. For example all the Cl_4 isomers are in the mass range 288–294 and all the Cl_7 in 390–396. Using the same principle a further 21 polychlorinated insecticides may successfully be determined in one test sample in addition to PCB.[64] With the same set of standards it is possible to determine PCB in soils by GC/MS with positive chemical ionisation.[65]

For the precise determination of the total PCB content in a sample it is necessary to determine all the PCB isomers present in it. It is necessary that each isomer appears on the chromatogram as a single peak well separated from other PCB isomers or compounds. This makes it possible to avoid dubious results from the variable contribution of co-eluting isomers in an unresolved peak and also from differences in sensitivity coefficients in the ECD. Consequently the precise determination of the total PCB content in test samples must be carried out with a set of all the individual PCB isomers as standards and not with mixtures. This is impossible in practice although all 209 PCB isomers have recently been synthesised and their retention times determined.[66]

Determination of the total content of PCB or of separate isomers by high resolution gas chromatography (HRGC)/ECD is carried out at present on capillary columns of SE-54 phase (DB-5, CP Sil 8, HP-5) of length 25–60 m. However all isomers encountered in

natural test samples cannot be completely separated on just one column. Nonetheless the relative elution order of PCB isomers has been determined.[62,66] With a fixed substitution pattern in the first ring the retention of this family of isomers increases in the orders: 2 < 3 < 4; 2,6 < 2,5 < 2,4 < 2,3 < 3,5 < 3,4; 2,4,6 < 2,3,6 < 2,4,5 < 2,3,4 < 3,4,5; 2,3,5,6 < 2,3,4,6 < 2,3,4,5. The relative elution order of the PCB isomers remains the same for polar phases such as OV 1701 etc.[62] It should be mentioned that the separation of PCB isomers on columns with phases SE-30, SE-54 and OV-101 differ a little depending on the column manufacturer. This is linked with different methods of surface deactivation prior to coating with a film and immobilising the film itself.

Complete separation of all PCB isomers in complex mixtures was successfully achieved only in 1988 using two-dimensional GC [67,68] carried out on a Sichromat-2 (Siemens), fitted with two independent ovens and two ECD (main and monitor). A chromatogram of the mixture of PCB isomers being analysed is obtained with the first column (SE-54, 25 m × 0.32 mm) in the first oven. The main portion of the eluate, corresponding to the part of the chromatogram with complete separation of isomers, is then passed through the monitor detector and selected fractions of the eluate, corresponding to the unresolved isomers on the chromatogram, are directed to the second column (OV-210, 30 m × 0.32 mm) in the second oven with the main detector. The monitor detector on the first column shows the usual gas chromatogram of a mixture by ECD except for one or several breaks, corresponding to the eluate fractions directed to the second column. The main detector on the second column shows chromatograms of the separated isomers in the fractions of the eluate directed from the first column. The principle of the method and the technical details have been described previously.[69]

The chromatographic separation of isomers on the second column may be very efficient. For example, the cluster of three isomers Nos. 126 (3,3',4,4',5-), 129 (2,2',3,3',5-) and 178 (2,2',3,3',5',6-) have retention times on the first column of 26.81, 26.80 and 26.85 min respectively and on the second of 37.98, 37.13 and 36.48 min, i.e. the unresolved triplet was separated into three separate peaks.[67]

Extremely important problems are the criteria for selection of standard PCB isomers for analysis as a function of the range of chlorine numbers (the number of chlorine atoms in the PCB isomers) and their contribution to environmental test samples, the use for calculation of the total PCB content, the relative distribution between various phases of natural aqueous media such as the atmosphere, water, sludges and biological specimens, aqueous and lipid solvents, the tendency to bind to particles and lipids, persistency and finally toxicity.

The first criterion, considering only a number of isomers covering a wide range of physicochemical properties, may be used for specific purposes such as a comparison between types of sample and regions and also for directing analyses. However choosing isomers, based on a range of chlorine numbers together with a requirement for their significant content in mixtures of the Arochlor type, for precise determination leads to a more or less arbitrary selection of isomers, at least in an ecological sense. The limitation of data by isomer is probably not the most correct approach for an answer to many problems linked with the behaviour and effects of PCB in the environment. Examples are the set of the ICES [?International Commission for the Exploration of the Seas (Ed. of Translation)] consisting of six isomers with chlorine numbers 3–7: No. 28 (2,4,4'-), 52 (2,2',5,5'-), 101 (2,2,',4,5,5'-), 153 (2,2',4,4',5,5'-), 138 (2,2',3,4,4',5-) and 180 (2,2,',3,4,4',5,5'),[68] a mixture of Arochlors 1221, 1016, 1254, 1262 (20:10:7:6) for the analysis of environmental samples,[70] a set of fourteen isomers: Nos. 28, 52, 74 (2,4,4',5-), 66 (2,3',4,4'-), 101, 151 (2,2',3,5,5',6-), 118 (2,3',4,4',5-), 153, 105 (2,3,3',4,4'-), 138, 187 (2,2',3,4',5,5',6-), 183 (2,2',3,4,4',5',6-), 156 (2,3,3',4,4',5-) and 180, comprising about 70% total PCB content in human milk.[71,72]

The set of PCB isomers based on their toxicity is important. Quantitative structure–activity relationships show that the most toxic PCB isomers are isostereomeric with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.[51,73] It is proposed that their toxicity is explained by the presence of chlorine atoms in positions 4,4' and/or 3,3,',5,5' and also by the possibility of two benzene rings achieving a planar configuration when one or both *ortho* positions are not substituted by chlorine atoms. This condition is satisfied by 13 isomers: Nos. 37 (3,4,4'-), 77 (3,3',4,4'-), 81 (3,4,4',5-), 118, 123 (2',3,4,4',5,5'-), 114 (2,3,4,4',5-), 105, 126 (3,3',4,4',5-), 167 (2,3',4,4',5,5'-), 156, 157 (2,3,3',4,4',5-), 169 (3,3',4,4',5,5'-) and 189 (2,3,3',4,4',5,5'-). It has been proposed that the toxicity of PCB isomers be considered the most important criterion for determining them in evironmental samples. Only four toxic isomers (Nos. 81, 114, 169 and 189) may be determined on one column of phase SE-54 and the remaining isomers may only be determined by two-dimensional GC.[68]

Mention must be made of the influence of the quality of appropriate PCB standards used on the precision of determining PCB isomers. PCB isomers of inadequate or inapplicable purity are available for sale. This leads to the development of additional peaks in the spectrum when working with an ECD or flame-ionisation detector (FID) and to the splitting of peaks on various columns. Consequently the use of calibration standards of mixed PCB solutions consisting of such individually inadequately pure PCB isomer standards may lead to large qualitative and quantitative errors when determining separate isomers and overall PCB content.[68]

IV. Herbicides

Chlorine-containing herbicides are widely used in agriculture for the elimination of weeds and undesirable woody undergrowth and as defoliants. The most important of them are acidic in character and consequently they are determined, as a rule, as esters by GC/ECD. Their determination by HPLC has only been described in the form of free acids in the concentration range 20 ng litre^{-1} to 1 mg litre^{-1}.[74]

Usually test samples of water[74–77] or sludge[77] are acidified to pH < 2 and the herbicide extracted with organic solvent, then esterified and the ester purified on columns of silica gel or Florisil.[75–77] Diazomethane[75] and pentafluorobenzyl bromide[76,77] are used as derivatising agents. The limits of detection of the methods are 0.05 μg litre^{-1},[76] 0.5 μg litre^{-1},[75] and 10–25 μg kg^{-1}.[77] Determination is carried out on packed[75,77] and capillary columns. It was shown that the choice between pentafluorobenzyl and methyl esters for the determination of herbicides depends on the relative importance of the detection limits and the linear range of concentration.[78]

The determination of 18 (cyanoethyl)dimethylsilyl derivatives of herbicides by the GC/N–P detector made it possible to exclude purification of the sample, which had been required for GC/ECD, and to have a limit of detection of 0.1 μg litre^{-1}.[79] The same method has been proposed for the determination of herbicides in solid discharges.[80] Capillary columns of length 30 m with phases DB-5 [76,78,80] and SP-2250 [78] and of length 15 m with phase DB-1 [79] have been used. The retention times, linear range of concentration

and sensitivity coefficients for herbicide esters have been determined for the separate columns.

V. Phenols

Polychlorophenols are some of the main contaminating substances in the environment, particularly pentachlorophenol which is the most widespread wood preserving agent, and is also a disinfectant and pesticide. 2,4-Dichloro- and 2,4,5-trichlorophenols are formed on breakdown of the widespread herbicides 2,4-D and 2,4,5-T and accumulate in nature. Trace quantities of polychlorophenols are determined as a rule in environmental objects as esters which are freed more easily from the interfering influence of other compounds and are separated on chromatographic columns.

Polychlorophenols are usually extracted from test samples of natural waters with organic solvents and are acetylated at the same time with acetic anhydride.[74–84] The same procedure is applied to sludges,[82] or polychlorophenols are first extracted and then acetylated.[85,86] The degree of extraction of chlorophenols from residues, however, depends markedly on the method used and consequently serious difficulties are encountered in the interpretation of the results obtained. This was shown when comparing methods of isolating chloroguaiacols and chlorocatechols from contaminated test samples.[87] From biosamples (homogenised tissue) chlorophenols are separated by a mixture of solvents with anydrous sodium sulphate[88] or dilute sulphuric acid.[89]

Chlorophenoxyacetates isolated from natural waters are not purified before determination but from sludges and particularly from biosamples they are usually separated from interfering organics on silica gel for example.[86,88] Test samples of chlorophenols are stored under the same conditions before analysis as when determining organochlorine pesticides.

Chlorophenoxyacetates are determined by GC/ECD on capillary columns of length 12–30 m with phases OV-73,[81,82] OV-1701 and SE-54,[85,88] OV-1 [86] and DB-1,[84] and by GC/MS with phases DB-1 [84] and SPB-5.[86] The limits of detection are 1 ng litre^{-1} for natural waters[81] and 0.2 ng litre^{-1} for sludges.[86] The limit of detection for chloroanisoles and -veratroles from a wet mass of fish tissue is in the range 0.2–10 ng g^{-1}.[88]

It was shown that the determination of chlorophenols in water as acetates has significant advantages compared with determination as pentachlorobenzyl ethers because the acetylation can be carried out directly in the test sample, reducing matrix influences and improving detection. By GC/MS it is possible to determine up to 35 haloesters from one test sample, including phenol and monochlorophenols which are usually difficult to determine by GC/ECD.[84]

In recent years the chromatographic and mass spectrometric properties of upwards of 30 chlorophenols and various esters have been studied in detail. Absolute limits of detection, relative retention times and sensitivity coefficients have been determined for chlorophenols (GC/ECD),[90] (GC/FID),[91] acetates (GC/ECD),[90] (GC/ECD, GC/MS),[84] anisoles,[90] pentafluorobenzyl ethers (GC/ECD),[91–93] (GC/ECD, GC/MS) [84] (cyanoethyl)dimethylsilyl ethers (GC/N–P-detector, GC/MS).[94] These data will permit the improvement and simplification of effective methods of determining chlorophenols in environmental objects in the near future.

Chlorophenols are rarely determined by other methods without derivatisation. They are usually separated from water and concentrated on solid adsorbents, such as polydivinylstyrene,[95] graphite [96] and XAD resins,[97] and then determined by HPLC on columns with C_{18} phases [95,96] or GC/IR spectroscopy.[97] Limits of detection are 4–40 ng litre^{-1}.[96]

VI. Dioxins and furans

Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) are tricyclic aromatic compounds with similar physical, chemical and biological properties. They are the reason for the mass illness and poisoning of people in Seveso (Italy) in 1976, Japan and USA in 1971–1983, and particularly at the time of the war in South Vietnam in 1968–1973.

The number of chlorine atoms in these compounds varies from 1 to 8 and the total number of positional isomers in PCDD and PCDF is 75 and 135 respectively (Table 1), they have been numbered systematically with indices D and F. For example the most toxic isomers 2,3,7,8-TCDD and 2,3,7,8-TCDF have the symbols D 48 and F 83 respectively.[98] All these isomers differ significantly in acute toxicity and biological activity (up to 300 000 fold). The most toxic and bioactive are 12 isomers with 4–6 chlorine atoms, of which 4 must be in positions, 2,3,7 and 8 (Table 2). Several of these isomers have oral LD_{50} levels < 10 μg kg^{-1} for guinea pigs.[99]

Table 1. Number of positional isomers of PCDD and PCDF.

Level of chlorine substitution	Number of isomers	
	PCDD	PCDF
Cl (mono)	2	4
Cl_2 (di)	10	16
Cl_3 (tri)	14	28
Cl_4 (tetra)	22	38
Cl_5 (penta)	14	28
Cl_6 (hexa)	10	16
Cl_7 (hepta)	2	4
Cl_8 (octa)	1	1
Total	75	135

Table 2. The most toxic PCDD and PCDF isomers.

PCDD	PCDF
2,3,7,8-Tetra-CDD	2,3,7,8-Tetra-CDF
1,2,3,7,8-Penta-CDD	1,2,3,7,8-Penta-CDF
1,2,3,6,7,8-Hexa-CDD	2,3,4,7,8-Hexa-CDF
1,2,3,7,8,9-Hexa-CDD	1,2,3,6,7,8-Hexa-CDF
1,2,3,4,7,8-Hexa-CDD	1,2,3,7,8,9-Hexa-CDF
	1,2,3,4,7,8-Hexa-CDF
	2,3,4,6,7,8-Hexa-CDF

PCDD and PCDF are found in trace concentrations in industrial chemical products such as polychlorophenols and their derivatives, and herbicides based on phenoxyacids and diphenyl ethers.

They are found in combustion products of industrial and communal incineration furnaces, on pyrolysis of PCB, chlorophenols, chlorobenzenes and many other chlorine-containing organic compounds.[100,101]

Modern methods for the quantitative determination of the isomers of PCDD and PCDF in environmental objects at concentrations at the ppt level will be considered in this chapter. Principal attention will be paid to the most toxic isomer, viz. 2,3,7,8-TCDD. Some of this material has been correlated in reviews.[100-102]

In view of the extremely low hazardous concentrations of PCDD and PCDF the quantitative content of their separate isomers may only be determined by HRGC and MS, since the former is capable of separating all isomers but is insufficiently selective with a background of matrix interference and the second identifies isomers and is extremely sensitive in the whole mass range at a level of 10^{-13} g on using high or low resolution mass spectrometry. However without HRGC, mass spectrometry does not resolve the majority of isomers because many of them give very similar mass spectra.[101,102]

1. Selection and storage of samples

Test samples of air containing PCDD and PCDF are taken in equipment consisting of sequentially connected filters for the removal of aerosols and cartridges of various adsorbents for trapping gaseous products. Glass fibre,[103-105] quartz wadding,[106] and as adsorbents XAD-2 resin,[105,107] polyurethane foam,[103,108] silica gel [104] and ethyleneglycol [106] are used as filters. A 6-1000 m^3 volume of air is passed through the filters and adsorbents under vacuum at a rate of 1-14 $m^3\ h^{-1}$.

In order to concentrate PCDD and PCDF from drinking water it has been proposed to pass the latter (10-200 litre) through a cartridge of XAD-2 resin [109] or C_{18} phase [110] at a rate of 0.15 to 0.5 litre min^{-1}.

Soil samples up to 3 cm from the surface layer and deeper layers are taken with tubular samplers and stored before analysis in wide mouthed glass jars with teflon screw caps at 4 °C [111] or −30 °C.[112]

After taking and before analysis biosamples must be rapidly frozen if possible and stored in the frozen state down to −180 °C, as a rule, in aluminium foil. This was shown for fish,[112-115] seals,[116] rabbits and pheasants,[112] human tissue [117-119] and vegetable fruit.[112] Temporary storage in the cold state is possible in glass vessels for test samples of cows' cream and earthworms (after washing and homogenisation).[112]

2. Preparation of samples for analysis and extraction

Samples need to be carefully homogenised and often dried for the quantitative recovery of PCDD and PCDF isomers from environmental samples using organic solvents.

Test samples of soil and sludges are dried in air or in a desiccator to constant weight at 60-110 °C and moisture content is usually determined. They are then screened through a sieve to remove foreign bodies (stones, shells, roots, etc.).[111,120-122] Test samples are also dried by mixing with anhydrous sodium sulphate [123-125] or by lyophilisation.[126]

Biological test samples are homogenised by alkaline,[112,113,118,127-129] acidic [115,129-131] or enzymic [132] degradation, lyophilisation and subsequent crushing,[129,133] grinding in a meat grinder or homogeniser with subsequent powdering with anhydrous sodium sulphate.[114,117,123,129,134-138]

For the complete identification and precise quantitative determination of PCDD and PCDF isomers it is necessary to introduce precise amounts of a mixture of isotopically labelled PCDD and PCDF standards. These are added to the homogenised test sample (biological tissue, soil, sludges, etc.) and to samples taken from various filters and to cartridges (from air and various types of water) before extracting them with organic solvent. The standards have a definite number of chlorine atoms including tetra- (T), penta- (Pe), hexa-, hepta-, and octa- (O)-CDD and -CDF, 10 isomers in all (0.1-3 ng of each). All the standards in Table 2 are used for the quantitative determination of all the most toxic isomers. The isotopically labelled standards $^{13}C_{12}$-PCDD/PCDF and less frequently $^{37}Cl_{4-8}$-PCDD/PCDF are generally used.[100-102,139] It should be mentioned however that these standards are very expensive. Consequently the whole set are used in only a few laboratories in the world. The majority use only a few standards which positively reduces the precision of determining and identifying PCDD/PCDF.

In addition to using filters for aerosols and cartridges for air, PCDD and PCDF are extracted from samples in a Soxhlet apparatus usually with toluene,[103-105,108] and from soils and sludges with various organic solvents or solvent mixtures.[111,121,122,124,125,140,141] It should be mentioned that the degree of recovery of PCDD/PCDF is increased by previous treatment of samples of soil, sludges and aerosols with hydrochloric acid prior to extraction or carrying out extraction combined with ultrasonic treatment.[142]

PCDD/PCDF are extracted from water with dichloromethane[125,141] and, after concentrating them on a cartridge with adsorbents, with acetonitrile or mixtures containing it.[109,110] PCDD/PCDF are extracted from homogenised biological samples such as fish tissue,[112-115,121,123-129,131,133,135,138] adipose tissue,[116-118,123,134,137,143,144] blood plasma,[119,144] milk [130,132,136,145] or human tissue [139] most frequently of all with hexane or mixtures of it with other organic solvents.

3. Purification of organic extracts

In addition to PCDD and PCDF, many other co-extracted substances and compounds of biogenic (lipids, proteins, etc.) and anthropogenic occurrence are contained in organic extracts of samples from environmental objects, which it is necessary to separate before determining dioxins and furans by GC/MS.

A multistage and very laborious purification of extracts is required when determining PCDD and PCDF by low resolution GC/MS (on packed columns). For example, extracts of human milk are purified on four chromatographic columns containing as adsorbents: 1) silica gel/alkali on silica gel/acid on silica gel; 2) silica gel/acid on silica gel; 3) silver nitrate on silica gel; 4) aluminium oxide and two columns of reversed and normal phase HPLC.[130]

The requirement for purification of organic extracts is reduced with the introduction of HRGC on capillary glass and particularly quartz columns with bonded phases and of length 30-60 m. It should be mentioned that purification methods vary strongly in relation to matrix complexity and in the case of biological samples it is necessary to purify extracts from far larger quantities of interfering substances and compounds than in the case, for example, of samples of atmospheric air.

After purification all the PCDD/PCDF isomers are concentrated as a rule on a column of carbon of type PX-21 (Amoco) or Carbopak (Supelco) from which they are eluted usually with toluene for analysis by GC/MS.

Extracts of air samples require simpler methods of purification. Their purification has been proposed on two columns of modified silica gel/silica gel and carbon on celite 545 [105] or aluminium oxide,[108] on a column of Florisil and normal phase HPLC,[103] on three columns with basic and acidic aluminium oxide and with activated carbon.[104]

Extracts of water, sludge and particularly biological samples, are usually subjected to complex and careful purification for determining the large number of individual isomers of various groups of PCDD and PCDF. Often however only 2,3,7,8-TCDD or other individual isomers or groups of isomers are determined. In this event the purification of extracts is significantly simplified. It must also be emphasised that it it possible to determine all PCDD and PCDF isomers from one fraction when purifiying extracts by adsorption column chromatography.[123] When using purification by normal or reversed phase HPLC in the last stage of purification several fractions must be used. Consequently these methods are usually used for determining separate isomers or groups of isomers.

Organic extracts of water are purified with conc. H_2SO_4 prior to decolourisation and on columns of Florisil and carbon/celite 545,[109] on columns of silica gel/acid on silica gel, of acid aluminium oxide and carbon/celite 545.[125]

Extracts of sludges are purified on columns of carbon/celite 545 and of silica gel with subsequent normal and reversed phase HPLC,[122] after removal of sulphur on columns of acid on silica gel, alkali on silica gel, $AgNO_3$ on silica gel, basic Al_2O_3, reversed phase HPLC,[126] exclusion chromatography, sequential treatment with Na_3PO_4, H_2SO_4, on columns of Al_2O_3 and carbon,[131] on columns of silica gel/Na_2CO_3/alkali on silica gel/H_2SO_4 with $CaSO_4$/silica gel/alkali on silica gel, acid Al_2O_3, carbon/celite 545 and neutral Al_2O_3.[121] Soils were purified as for water,[125] on columns of CsOH/silica gel/acid on silica gel and on Al_2O_3,[111] contaminated soil on columns of CsOH/silica gel/acid on silica gel and $AgNO_3$/silica gel.[111]

It has been proposed to purify extracts of fish tissue on columns of MgO/celite 545/Al_2O_3 and Florisil/Al_2O_3,[133] on a column of acidic Al_2O_3/basic Al_2O_3 and then by normal and reversed phase HPLC,[128] on three columns of H_2SO_4/silica gel, NaOH/silica gel or $AgNO_3$, basic Al_2O_3 and reversed phase HPLC,[115] by exclusion chromatography and reversed phase HPLC on two different columns,[127] by exclusion chromatography and on columns of Al_2O_3 and Florisil,[138] on four columns with H_2SO_4 and NaOH with silica gel and by HPLC,[112] on three columns of celite 545/conc. H_2SO_4, Cs_2SiO_3 and carbon,[114] and on columns of silica gel/K_2SiO_3/H_2SO_4/celite 545, Al_2O_3, carbon/silica gel [135] as in the case of sludges.[121,131]

Extracts of human tissue samples are purified by treatment with H_2SO_4, on columns of Florisil and carbon/silica gel,[139] adipose tissue on three columns of silica gel/alkali on silica gel/acid on silica gel, $AgNO_3$/silica gel, basic Al_2O_3 and then normal and reverse phase HPLC,[146] on three columns of acid on silica gel, Al_2O_3, carbon/celite,[117] by exclusion chromatography on columns of Florisil and of carbon,[143] by exclusion chromatography on columns of Florisil, Al_2O_3 and carbon/celite 545,[116] by treatment with H_2SO_4, on columns of silica gel, carbon/silica gel, by GC,[118] human blood plasma on columns of acid on silica gel/silica gel and carbon/celite 545,[144] as for adipose tissue,[119] and human milk by a modified procedure [136] for adipose tissue.[146]

Among the contemporary methods of preparing samples and analysing by GC/MS a procedure has been evolved combining the extraction and purification of samples of soil, sludges and biological specimens into a two stage process and enabling determination of all the PCDD and PCDF isomers from one fraction.[123] In the first stage the mixture of homogenised test sample and Na_2SO_4 is extracted in the first column and the extract passed in the same column through K_2SiO_3/silica gel, and then through two columns of Cs_2SiO_3 or K_2SiO_3/silica gel and activated carbon. With the exception of *ortho*-PCB, the PCDD, PCDF, polychlorinated naphthalenes (PCN), biphenyls (PCBP) and a series of polyaromatic hydrocarbons remain on the carbon adsorbent. In the second stage the extract is passed through two columns of Cs_2SiO_3/acid on silica gel and aluminium oxide. Modifications of this procedure have been applied successfully to the determination of PCDD/PCDF isomers in human adipose tissue,[134,144] and also in human and cows' milk.[145,147]

It is evident from the material presented above that the purification of extracts for subsequent determination of PCDD and PCDF by GC/MS is a complex and prolonged process in the majority of cases. The main part of the time is consumed in this way, occasionally reaching 80% (10 h or more) of the time for carrying out the whole analysis. Consequently attempts have been made to reduce the time of purification of extracts for which a modified method of separation and identification by GC/MS/MS has been proposed.[109,148–150]

The method of tandem mass spectrometry is based on the separation of the components of a mixture according to their molecular weight in the first analyser of the mass spectrometer (low or high resolution) and obtaining structural information on the determined compounds in the second analyser at low resolution. It is impossible to use these separating capabilities of the MS/MS method for the direct analysis of extracts in view of the extremely low concentrations of PCDD and PCDF in comparison with the main interfering compounds. Consequently it is necessary first to remove the latter from the compounds to be determined on short capillary gas chromatographic columns of length 12 m. This method has been used successfully for determining PCDD and PCDF in drinking water and soil and has enabled the time required for purification of extracts of biological samples to be reduced significantly by shortening several stages.

4. Gas chromatographic separation of isomers

Purified extracts of PCDD and PCDF are most frequently analysed by gas chromatography-mass spectrometry with quartz and, far more rarely, with glass capillary columns, usually 50–60 m long with a strongly polar (3-cyanopropyl)polysiloxane phase, such as SP-2330,[135,138,145] SP-2331,[105,126,136,144] CP-Sil 88 [118,125] and Silar 10C,[151] and with non-polar phase DB-5.[116,124,143,145–147] Columns of length 25–30 m with DB-5 have also been used.[116,135,137,139] The columns lead directly into the ion source of the mass spectrometer operating in electron impact (EI) or negative chemical ionisation (NCI) modes.

It must be emphasised however that at the present time a single column does not exist in which it would be possible to separate all the 2,3,7,8-substituted PCDD/PCDF isomers in the presence of all the PCDD/PCDF isomers. It is possible to separate all the 2,3,7,8-substituted isomers of PCDD successfully on columns of SP-2330 [151] and Silar 10C,[152] but in the case of the 2,3,7,8-substituted isomers of PCDF this proved to be impossible even within the TCDF group.[153,154] In the latter case complete separation was achieved only when using two columns such as SP-2331 and DB-17,[155] or on a column of a new smectic liquid crystal phase.[156]

The use of sequential combined columns of DB-5 and CP-Sil 88 of length 50–60 m must be mentioned. The various chlorine groups of PCDD/PCDF with equal numbers of chlorine atoms are separated on the first column and the isomers in these groups in the second. Such a method enables large volumes of solvent, up to 10 μlitre, to be injected into the gas chromatograph and significantly reduces the level of detection.[137]

Gas chromatographic characteristics have been described for all TCDD-OCDD for a Silar 10C column,[152] all PCDF for a DB-5 column,[157] for 35 PCDF for SP-2330 and V-101 columns,[158] for all TCDF for DB-5 and SP-2331 [154] and SE-54 and SP-2330 columns,[153] all TCDD for SP-2330 and OV-1 columns[159] and for columns with modified (cyanopropyl)polysiloxane phase,[160] and for the toxic PCDD/PCDF for columns with the new OV-240-OH phase.[161]

5. Mass spectrometric determination

The mass spectrometry of PCDD and PCDF has been described in detail in reviews[100–102,151,162,163] and will be considered here only briefly and as applied to the quantitative determination of isomers of xenobiotics in the environment.

Table 3. Ions (m/z) used for monitoring PCDD and PCDF in test samples of environmental objects.[101]

Ions for monitoring		Tetra-	Penta-	Hexa-	Hepta-	Octa-
	PCDD					
EI	M^+	320	354	388	422	—
	$(M+2)^+$	322	356	390	424	458
	$(M+4)^+$	—	—	—	—	460
NCI	M^-	(320)	354	—	—	—
	$(M+2)^-$	(322)	356	—	—	—
	$(M-Cl)^-$	—	—	353	387	—
	$(M+2-Cl)^-$	—	—	355	389	423
	$(M+4-Cl)^-$	—	—	—	—	425
	PCDF					
EI	M^+	304	338	372	406	—
	$(M+2)^+$[a]	306	340	374	408	442
	$(M+4)^+$[a]	—	—	—	—	444
NCI	M^-	304	338	372	406	—
	$(M+2)^-$[a]	306	340	374	408	442
	$(M+4)^-$[a]	—	—	—	—	444

[a] PCN and PCT intefere a little, but interference from PCDPE is possible.

Low resolution quadrupole mass spectrometry is most frequently used for monitoring PCDD and PCDF. EI in the selective ion detection (SID) mode is used for the determination of TCDD/TCDF for which it has a high sensitivity (1–10 pg). However the sensitivity falls significantly for the more chlorinated isomers. On the other hand NCI in the SID mode is 1–2 orders of magnitude (10–100 fg) more sensitive, when using methane as carrier gas, for all the PeCDD-OCDD and TCDF-OCDF in comparison with EI but has a low sensitivity for all TCDD, only 20% of that for EI.

PCDD/PCDF ions used for monitoring in EI are M^+ (for tetra-, penta- and hexa-) and $(M+2)^+$ for hepta- and octachloro compounds, in NCI M^- for the less chlorinated isomers of PCDD and M^- and $(M+2-Cl)^-$ for the more chlorinated isomers. For PCDF M^- or $(M+2)^-$ (Table 3) are used.[101]

The use of high resolution mass spectrometry (5000–10 000) gives additional selectivity and the senstivity on EI in the SID mode may reach 10–200 fg for all TCDD(F)-OCDD(F). The use of high resolution mass spectrometry and of MS/MS for determining PCDD/PCDF isomers has been described in detail in a review.[102]

The quantitative determination of PCDD/PCDF isomers is based on measurements of peak area or height and comparison of them with calibration graphs of external standards and isotopically labelled internal standards. Introduction of the latter into test samples before extraction of PCDD/PCDF helps to explain their loss in the extraction process and in the purification of extracts. It also aids identification of isomers and their quantitative determination.

Table 4. Molecular ions of PCDD and PCDF.[101]

Molecular ions (m/z, M^+, M^-) (chlorination)	Compounds					
	PCDD	$^{13}C_{12}$-PCDD	^{37}Cl-PCDD	PCDF	$^{13}C_{12}$-PCDF	^{37}Cl-PCDF
Mono-	218	230	220	202	214	204
Di-	252	264	256	236	248	240
Tri-	286	298	292	270	282	276
Tetra-	320	332	328	304	316	312
Penta-	354	366	364	338	350	348
Hexa-	388	400	400	372	384	384
Hepta-	422	434	436	406	418	420
Octa-	456	468	472	440	452	456

The following are necessary[101] for proof of identity of PCDD/PCDF isomers. The retention time of the PCDD and PCDF isomers being determined must be within 3 sec to establish the isomeric specificity and must be confirmed daily. The signal to noise ratio must be at least 2.5:1. The chlorine cluster must be ±10% of the theoretical value and precise fragments, such as $(M-COCl)^+$ ions, must coincide with the precise chlorine cluster.

In spite of the use of fairly effective methods of purification of extracts the presence is occasionally encountered of other contaminating polychlorinated compounds interfering with analysis. These may be mainly non-*ortho*-substituted PCB, PCN, PCBF, polychlorinated terphenyls (PCT), diphenyl ethers (PCDPE), pyrenes (PCP) (Tables 4 and 5) and also occasionally polychlorinated anthracenes, phenanthrenes and fluorenes. These compounds however are usually readily distinguished by their intense M^+ or M^- ion and the number of chlorine atoms deduced from their ionic clusters. In rare cases polychlorinated benzenes, benzofurans and styrenes are observed, but they do not interfere with the analysis.[101]

Methods of analysis of trace quantities of PCDD/PCDF have improved markedly in recent years and this permits a significant reduction in their limits of detection. They are, for example (depending on the isomers), for samples of air 0.01–0.05 [105] and 0.1–1 pg m^{-3},[103] sludges (for TCDD) 0.1 ng kg^{-1},[126] drinking water 1 pg $litre^{-1}$,[109] blood plasma 0.003–0.02 [144] and 1.25 pg $litre^{-1}$ (for TCDD),[119] adipose tissue 2–10 ng kg^{-1},[139] milk 0.1–0.5 [147] and 0.2–0.4 ng $litre^{-1}$.[145]

Table 5. Molecular ions of polychlorinated compounds present in environmental test samples and possibly interfering in the mass spectrometric analysis of PCDD and PCDF.[101]

Molecular ions (m/z, M^+, M^-) (chlorination)	Compounds					
	PCBF	PCB	PCN	PCT	PCDPE	PCP
Mono-	186	188	162	265	204	236
Di-	220	222	196	298	238	270
Tri-	254	256	230	332	272	304
Tetra-	288	290	264	366	306	338
Penta-	322	324	298	400	340	372
Hexa-	356	358	332	434	374	406
Hepta-	390	392	366	468	408	440
Octa-	424	426	400	502	442	474
Nona-	—	460	—	536	476	508
Deca-	—	494	—	570	510	542

6. Safety techniques when carrying out analyses

It is necessary to take special safety measures when carrying out analyses because of the extreme toxicity of many isomers of PCDD and PCDF. These begin at sample taking and end with the decontamination of the waste water after carrying out analyses.[164]

When taking samples of environmental objects precautions depend strongly on the concentrations of PCDD/PCDF presumed to be present. In the case of strongly contaminated places of sampling and of the samples themselves special safety measures must be applied which are linked with the organisation of decontamination areas, special clothing, etc. In uncontaminated places test samples of PCDD/PCDF are collected with the same precautions as when taking samples of other highly toxic xenobiotics for analysis.

The selected samples are carefully packed and transferred to the station laboratory. Each test sample of soil and sludge in glass beakers with teflon screw lids is placed in a plastic container which is itself placed in a metal container with kieselguhr. Biological samples are wrapped 2–3 times in aluminium foil and transferred in the frozen state in foam-plastic containers. Water samples in glass bottles are first placed in a plastic container with kieselguhr which is then put into a metal container with kieselguhr.

All work must be carried out in the station laboratory in a fume cupboard. Liquid waste water must be mixed with methanol or ethanol and irradiated with UV light at a wavelength > 290 nm for several days. Residues of samples coming out of a chromatograph and GC/MS sample effluent must be passed through a column of activated charcoal or bubbled through a trap of oil or high boiling alcohol.

Working surfaces and equipment in a station laboratory are sampled periodically with pieces of filter paper to determine their cleanliness. This is considered satisfactory at a content of 1 μg 2,3,7,8-TCDD in the wipe sample. At >1 μg the location must be cleaned and at >10 μg there is a threat of contamination and consequently working places must be cleaned meticulously.

The problems arising after the accumulation in nature of a large number of highly toxic chlorine–containing xenobiotics oblige mankind to solve a most complex analytical problem, viz. to develop methods for the quantitative and qualitative determination at the ppt level of polycyclic mixtures in various natural objects. This requires highly pure, and frequently ultrapure, organic solvents, inorganic acids, adsorbents and other chemical reagents, expensive high purity standards for compounds and the isomers to be determined, chromatographs with capillary columns and gas chromatograph-mass spectrometers of high (6000–10 000) resolution with modern systems for processing the results obtained. For the safe determination of complex mixtures of dioxins and furans exceptional cleanliness of laboratory premises is required, to the level for carrying out genetic engineering work, there are very stiff requirements for safety techniques and high qualifications are needed for the scientific and service personnel. The combination of these necessary conditions has a strong influence on the cost of analysis of the first sample, from several tens for determining insecticides to SUS 3000 for the isomerically specific determination of dioxins and furans in biological samples.

Nonetheless the large material outlay in developed countries on the bulk analysis of polychlorinated compounds, particularly the most toxic isomers of dioxins, furans and biphenyls in environmental samples, and, which is very important, in human milk, adipose tissue and blood plasma is considered necessary since these xenobiotics are one of the main sources of progressing immunodeficiency of higher organisms, similar in character to the immunodeficiency caused by the AIDs virus.

In the last five years the industrially developed countries have joined in the need to increase the sensitivity of methods of determining analytically down to a level of 1 ppq (pg kg^{-1}) for 2,3,7,8-TCDD. Only in this case does it seem possible to assess admissible levels for these xenobiotics for the developing foetus and the newborn and to solve many practically important problems including a check on the purity of childrens' food. There is no doubt that the solution of this problem reduces in principle to new technology in ultramicroanalysis.

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Dioxins: analytical chemical aspects of the problem

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ABSTRACT. The dioxins are a large set of polyhalogenated polycyclic compounds formed as impurities during many types of production using chlorine, bromine and their compounds. These xenobiotics have no equals among other contaminants in their danger to man and in global ecological effects. The current status of some aspects of the problem of dioxin and related compounds is considered using material from the foreign scientific press. Data are presented on the physicochemical and other properties of dioxins. Information is correlated on the main sources of dioxins and on the methods of determining them in the environment and the biosphere (air, soil, water, biological samples, etc.). Problems considered are the contamination of the environment, monitoring, ways of reducing the danger and the prevention of dioxin contamination.

The bibliography contains 563 references.

Contents

I. Introduction 1063
II. Physicochemical properties of dioxin-type xenobiotics 1065
III. Sources 1067
IV. Toxicity. Medical effects and their consequences 1070
V. Determination of xenobiotics of the dioxin type 1074
VI. Environmental contamination by xenobiotics of the dioxin type. Monitoring 1078
VII. Prevention and destruction of dioxin contamination 1081

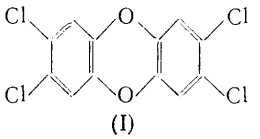
I. Introduction

In the last 15–20 years, one more ecological hazard has been added to the vast total threatening civilisation, viz. the possibility of planetary poisoning of our habitation by dioxin and compounds related it.[1–114] Dioxin and the numerous group of dioxin-like substances are foreign to the living organism (xenobiotics) and enter the biosphere from the production or discharges of numerous technologies. In contrast to the mass of other xenobiotics such as organochlorine pesticides *dioxins are never the desired product* of human activity. They only accompany it as microimpurities.[50] Consequently the negative actions of dioxin microimpurities on the living matter of the planet remained unnoticed against the background of the action of thousands and millions of tons of other technogenic discharges for many decades. However this dioxin microimpurity, characterised by a complex of unusual physicochemical properties and unique biological activity, may become a source of the most dangerous lasting contamination of the biosphere, significantly more serious than its contamination by many other substances such as the organochlorine pesticides.[94]

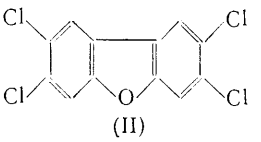
This is because in the last 50–60 years dioxins and related compounds have been generated continuously and on ever increasing scale by civilisation, discharged into nature and have accumulated there. The process of accumulation of these xenobiotics in the biosphere knows no saturation limits or national boundaries. At the present time the situation is such that the concentration of dioxins in the hydrosphere and lithosphere may reach critical values and disease of living matter may assume an irreversible character.

The history of the 'acquaintance' of mankind with dioxins arose in 1930 when the development of the manufacture and use of polychlorophenols led to an increase in the *occupational disease chloroacne* (relapsing inflammation of the sebaceous glands), although the illness itself had been known since 1899.[50,88–93] The geographical distribution of chloroacne spread significantly in 1940–1950 linked with the creation of large tonnage manufacture of 2,4,5-trichlorophenol and also of the manufacture of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) obtained from it, of the antibacterial preparation hexachlorophene, etc. Many cases of poisoning of personnel in this industry during operations have been described, some as a result of accidents.[17,38,88] It has recently been shown that recurrences of chloracne in many of those affected have developed even 20–35 years after the disease.[90]

The source of these diseases was established in 1957 by several groups of investigators simultaneously.[115–117] It turned out to be 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) (I) formed as a microcontaminant when making 2,4,5-trichlorophenol (TCP).[115–116] Passing with the latter into technological chains and then into the final product (herbicides, antibacterial preparations, etc.) dioxin (I) sets in motion, as clarified recently, not only the disease chloracne, but also others including acute poisoning.[93,118,119]



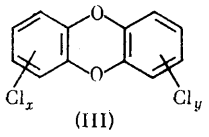
(I)

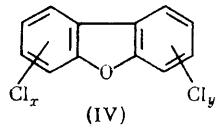


(II)

2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF) (II) was also postulated, simultaneously with dioxin (I), as a chloracnogenic factor.[117] However particular attention has been drawn to this xenobiotic itself as a microcontaminant in polychlorobiphenyls (PCB) used as liquid dielectrics, heat-transfer agents, hydraulic fluids, etc. The massive poisonings caused by xenobiotic (II) (in 1968 in Japan[120] and in 1979 in Taiwan[121]) were linked with the entry of PCB into rice oil which led to the so-called Yusho illness (acute liver poisoning acocmpanied by many side effects).[95,96]

It has been shown that xenobiotics (I) and (II), like many other examples of polychlorinated dibenzo-*p*-dioxins (PCDD) (III) and dibenzofurans (PCDF) (IV), have similar toxicological characteristics.[122]

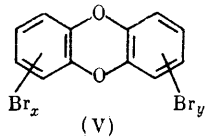

(III)

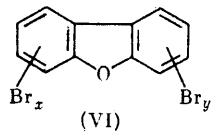

(IV)

$n = x + y = 1$ to 8

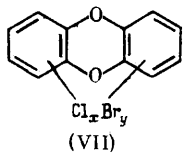
The presence of micro contamination by (III) and (IV) in the products of chloro-compound manufacture is the reason for many cases of poisoning in the sixties, seventies and even the eighties.[17,23,93,96,97] Their entry into chicken feed has repeatedly caused much damage to the broiler industry.[123] Poisoning of people and extended contamination of various objects by xenobiotics (III) and (IV) has been observed many times in the non-industrial sphere as well, for example in the inadvertent utilisation of effluent from chloro-compound manufacture,[66,67,70,71] in poisoning at electric power plants, where much polychlorovinyl insulation material is concentrated or there are transformers (capacitors) packed with PCB.[47,88,124,125]

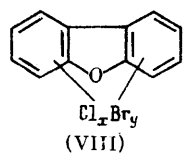
It has been established recently that polybromo-[126–129] and mixed polybromochloro-containing[130,131] dibenzo-*p*-dioxins and dibenzofurans of structure (V)–(VIII) are not less but in some cases more dangerous than the polychlorinated derivatives (III) and (IV). These are formed as byproducts in the manufacture of organic halides, on burning fuel in the presence of bromine compounds and also on processing or the destruction of industrial and domestic refuse.


(V)


(VI)

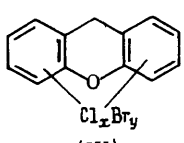
$n = x + y = 1$ to 8

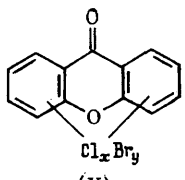

(VII)

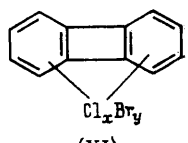

(VIII)

$n = 1$ to 8

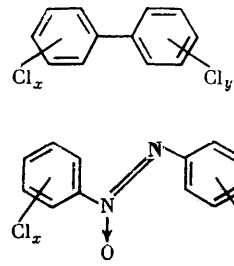
Many other organohalogen compounds possess the biological activity characteristic of dioxin (I). These include certain tricyclic compounds such as polychloro-, polybromo- or polychlorobromo-containing xanthenes (IX), xanthones (X) and biphenylenes (XI)[55,132,133] and also the structurally more complex polychlorinated quaterphenyls.[95,96,134]


(IX)


(X)


(XI)

Finally a series of bicyclic compounds such as polychlorobiphenyls,[95,96] polychloroazo- and polychloroazoxybenzenes[135] should also be included.

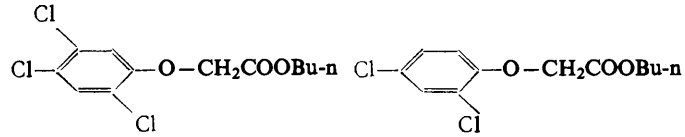


Many of the tri- and bicyclic compounds indicated accompany chemical production and are precursors of xenobiotics (III) and (IV) in nature.

In the industrially developed nations the attention of investigators was drawn long ago to the danger of permanent contamination of the biosphere with dioxin and related xenobiotics. This is evidenced by the appearance of numerous monographs, symposia, scientific conference proceedings,[1–43] reviews[44–114] and dissertations[136–145] devoted to individual aspects and to this problem as a whole. Since 1980 international cooperation has been effected within the framework of annual international scientific conferences devoted to the dioxin problem.[25–34] In several countries the problems linked with dioxins occupy one of the most important places in state ecological and ecologo-economic programmes.

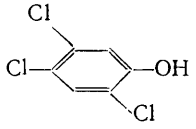
In the last two decades the problems of contaminating the biosphere with dioxins have been widely discussed by the public, in political circles and in the press. This was made possible by the active exposure of the material from two massive events in the years 1960–1970.

One of these was the war of the *USA in Vietnam* in which ~57,000 tons of the herbicide 'Agent Orange' containing (according to official data) about 170 kg dioxin (I) was applied to the territory of South Vietnam during 1962–1970.[35–41,72] The numerous communications generated on the massive disease of the population of this region and the participants of the war,[39,50,66,72,146–149] the negative effects of the herbicide on the child-bearing function of the women, its teratogenic action[146,147] and the more remote consequences of the disease[11,18,24] could not fail to cause alarm since the components of herbicide 'Agent Orange' [a mixture of the butyl ester of 2,4,5-trichlorophenoxyacetic acid, 2,4,5-T (XII), containing (I) as a contaminant, and the butyl ester of 2,4-dichlorophenoxyacetic acid (XIII)] were widely used in agriculture.


(XII) (XIII)

The other occurrence proved to be an *industrial incident* happening in July 1976 *in Seveso* (Italy).[67,69,99,100,106,150–156] At the ICMESA works the discharge took place, as a result of an accident,

of hundreds of tons of 2,4,5-trichlorophenol (XIV) which was accompanied by the discharge of dioxin (I) and other xenobiotics of the type of (III) and (IV).



(XIV)

No less than 500 people suffered drastically from contamination by the noxious cloud in the neighbouring territory. Several thousand residents of neighbouring small villages were subjected to the action of dioxin, thousands of domestic animals perished. It was considered that from 2 to 3 kg, according to some assessments up to 5 kg, dioxin was dispersed as a result of the accident. It is difficult to know the amount more precisely since the procedures of the seventies did not permit complete recovery of dioxin from the samples analysed.[154]

Both these occurrences and also cases, less known to the wider public, of contamination of land such as in the state of Missouri (USA),[66,67,70,71,157,158] revealed the horrible perspective of remote consequences of global contamination of the biosphere by xenobiotics of the dioxin type. This could not fail to exert psychological pressure on mankind and led to increased attention to dioxin as the source of possible global ecological disaster, in principle more serious and immeasurably more dangerous than the multiton discharge of other contaminants.

The analytical chemical aspects of the problem of dioxin and related compounds are considered briefly (chiefly from foreign published material) in the present review. Problems of the physicochemical and medico-ecological characteristics of dioxins, some technological problems, etc. are also considered in part. Attention is mainly paid in the present review to the contaminants which are most widespread in nature, viz. chlorinated dibenzo-*p*-dioxin (III) and dibenzofuran (IV), from the sum total of xenobiotics (III)–(XI) and the corresponding bicyclic compounds.

II. Physicochemical properties of dioxin-type xenobiotics

Resolution of the practical problems of the organic analysis of xenobiotics (III)–(VIII) is complicated appreciably by the problem of their *isomer composition*. Thus the archetype of all the substances, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (I), is only one of the 22 possible isomeric tetrachlorodibenzo-*p*-dioxins. Equally 2,3,7,8-tetrachlorodibenzofuran (II) is only one of the 38 possible isomeric tetrachlorodibenzofurans. Altogether the total of uniformly substituted polychloro- or polybromodibenzo-*p*-dioxins and dibenzofurans comprises 420 individual substances. The isomer composition of mixed chlorobromo-containing xenobiotics (VII) and (VIII) is even more abundant.

Data on the complete isomeric composition of xenobiotics (III)–(VIII) are correlated in Table 1.[130] To complete the picture, data on compounds (IX)–(XI) are also included although the xanthenes and xanthones at present are not important for natural processes and the biphenylenes are converted into compounds (III) and (IV). As was shown in the last decade, practically all of the 5020 substances of classes (III)–(VIII) may form part of microdischarges of modern technology. Only tetra- to octa-substituted (III)–(VIII) containing halogen atoms in positions 2,3,7,8 are highly dangerous to man and nature. There is obviously an order of difficulty in the analytical chemistry connected with the need to identify and estimate the tens or hundreds of xenobiotics most dangerous to the environment among thousands of similar substances.

Table 1. Number of homologues and isomers in families of tricyclic halogen-containing xenobiotics (III)–(VIII) and in compounds (IX)–(XI) as a function of the number of chlorine and/or bromine atoms in the molecule.

$n=x+y$	Number of isomers								
	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)
1	2	4	2	4	0	0	8	8	4
2	10	16	10	16	14	28	60	60	34
3	14	28	14	28	84	168	224	224	112
4	22	38	22	38	254	496	572	572	298
5	14	28	14	28	420	840	896	896	448
6	10	16	10	16	452	880	912	912	472
7	2	4	2	4	252	504	512	512	256
8	1	1	1	1	74	134	136	136	76
Total	75	135	75	135	1550	3050	3320	3320	1700

Further complexity in the organisation of analysis may be explained by the presence in microdischarges from existing technology of functionally substituted xenobiotics (III)–(VIII) containing NO_2, NH_2, Alk and other groups in place of halogen. These are highly dangerous substances in several cases. Among them, and among (III)–(VIII), competitive antagonists of the highly toxic xenobiotics are encountered which reduce the effect of the latter.[132,159–161] This may also lead to an increase in the volume of analytical work and in its complexity as a result of a wider background and limitations on the use of biological methods of analysis.

Difficulties arising in connection with the broad isomeric composition of xenobiotics (III)–(VIII) are also caused by inadequate measurements of physical and chemical properties in series of regioisomers. The physical properties of the xenobiotics are determined mainly by their overall chemical nature, including the number of halogen atoms in the molecule, and the chemical properties also depend essentially on the positions of halogen atoms. Correspondingly regioisomers differ appreciably in biological activity and in their rate and route of metabolism in nature. Both bioactivation and biodegradation of compounds (III)–(VIII) are possible in nature.[162–164] Thus xenobiotics (III)–(VIII) constitute a system of contamination of nature which is not only complex but also changing constantly in direction and time.

Three groups of properties are particularly important for practical analytical chemistry. First there are properties determining the limiting content of xenobiotics in various phases (water, soil and air),

then properties governing the form of their existence and behaviour in these phases and finally properties controlling the behaviour of xenobiotics at phase boundaries (air–water, soil–water, water–octanol, phase–living organism).[44,45,73–75,165–195] Certain physicochemical characteristics of compounds of the (III) family, derived from published data,[45] are correlated in Table 2. These also permit opinions to be formed on the properties of xenobiotics (IV)–(VIII) [some properties of compounds (IV) are given[141]]. It follows from the data presented that such key properties of xenobiotics (III) as solubility in water, distribution coefficient in the octanol–water system (K_{OW}) and vapour pressure (P^S) do not change regularly with increasing number of chlorine atoms in the molecule.

Characteristically dioxin (I) and also the corresponding furan (II) are crystalline substances with melting points 305[45,49,196] and 227–228 °C[141] respectively. The other tetrachloro derivatives (III) and (IV) are also high melting. A lower melting point is characteristic for the less chlorinated compounds (III) and (IV).[45,141]

The good solubility of various (III) derivatives in organic solvents is determined by the *lipophilic* (hydrophobic) nature of these nonionic organohalogen compounds. In particular the solubility of dioxin (I) is (in g litre^{-1}) 0.57 in benzene, 0.37 in chloroform, 0.11 in acetone and 0.05 in octanol.[196] At the same time these xenobiotics are practically insoluble in water (2.10^{-7} g litre^{-1}).[196] It must however be stressed that, as recent measurements have shown, under practical conditions the solubility of dioxin (I) in water may be both less[169] and significantly greater[170] than that measured initially in double distilled water.[196] This is explained by the high capability of (I) towards complex formation with water-soluble polymers.[183] These latter substances, such as humic and fulvic acids, are absent from super-pure water,[170] however they are present under actual conditions of analysis. Derivatives of the (IV) series are just as poorly soluble in water as those of the (III) series.[197]

The *volatility* of the xenobiotics under consideration is usually insignificant.[45] For example the vapour pressure of dioxin (I) under ideal conditions is 1.7×10^{-6} mm Hg.[49,196] However even in 1973 it was reported that (I) may actually be present in air at a 'supersaturated' concentration,[198] which is caused by its effective adsorption on various aerosol particles.

It follows from these data that the actual concentrations of (I) determined by analysis in two most important phases, viz. air and water, may prove to be greater than the concentration determined by the physicochemical characteristics, volatility and solubility, obtained under ideal conditions. In addition the transport of xenobiotics in these media is not subject to such an extent to the rules of gas dynamics or true solutions. How much is determined by the behaviour of their carriers, aerosol particles in the air and molecular complexes in soil and water?

Two other physicochemical characteristics of the xenobiotics under consideration are analytically and toxicokinetically important. These are the *high adhesive ability* in relation to different types of evolved surface, including soil, ashes, residues, etc.[166,199,200] (this property depends appreciably on the presence of other organic substances in the material[166,179]) and the *high distribution coefficient in the octanol–water system* (Table 2).[178] In reality these two properties determine the special behaviour of xenobiotics in the environment and their entry into living matter.

It is known for example that in inanimate nature xenobiotics (III) and (IV) gradually transfer into the organic phase of soil or water migrating onwards as complexes with organic substances (they pass into the air, reservoirs, and are incorporated into food chains).[165–181] Having entered into living organisms xenobiotics accumulate in them (bioconcentration).[182–195] It has been proposed that the coefficient of *bioconcentration* (BCC) is linked with the distribution coefficient in the octanol–water system by a simple relationship[184,185] (value of BCC are given in Table 2 and were calculated with the aid of the

Table 2. Some physicochemical characteristics of polychlorobenzo-*p*-dioxins (III).

Compound	Mp, °C	Water solubility, ng litre^{-1}	lg K_{OW}	Vapour pressure P_L^S, Pa	Henry constant, Pa m^3 mol^{-1}	Molar volume, cm^3 mol^{-1}	Predicted log BCC
2-Cl-DD	105.5	278 000 (25° C)	4.94	$8.58 \cdot 10^{-2}$	14.82	212.9	3.52
2,3-Cl_2-DD	164.0	14 900 (25° C)	4.70	$9.26 \cdot 10^{-3}$	6.61	233.8	3.34
2,8-Cl_2-DD	151.0	16 700 (25° C)	4.70	$2.47 \cdot 10^{-3}$	2.13	233.8	3.34
1,2,4-Cl_3-DD	129.0	8 410 (25° C)	6.45	$1.07 \cdot 10^{-3}$	3.84	254.7	4.67
2,3,7,8-Cl_4-DD	305.0	19.3 (22° C)	7.02	$5.79 \cdot 10^{-5}$	3.34	275.6	4.82
1,2,3,6-Cl_4-DD	219.0	320 (20° C)	7.13	$5.81 \cdot 10^{-5}$	0.71	275.6	5.19
1,2,3,4,7-Cl_5-DD	196.0	118 (20° C)	7.44	$4.31 \cdot 10^{-6}$	0.264	296.5	5.42
1,2,3,4,7,8-Cl_6-DD	273.0	4.42 (20° C)	7.79	$1.45 \cdot 10^{-6}$	4.52	317.4	5.69
1,2,3,4,6,7,8-Cl_7-DD	265.0	2.4 (20° C)	8.20	$1.77 \cdot 10^{-7}$	0.133	338.3	6.00
Cl_8-DD	332.0	0.4 (20° C)	8.60	$1.19 \cdot 10^{-7}$	0.683	359.2	6.31

proposed expression log BCC = 0.76 K_{OW} − 0.23[185]). However, the experimental values of BCC for xenobiotics (III) and (IV) in animals or in plants (for example in fish values of BCC vary from 2000 to 6000[188]) proved to be significantly lower than might have been expected[165] proceeding from data on the distribution coefficients of xenobiotics in the octanol–water system and on their water solubility. This is explained by the substantial influence of the biochemical special features of the accumulating organisms on the degree of absorption and the retaining ability for xenobiotics and also on the substantial difference of the properties of pure xenobiotics from the properties of their actual adducts with organic substances taking part in biotransfer.[181–183,186]

One of the analytically important characteristics of compounds (III) and (IV) is their extreme *chemical stability* in acid and alkaline solutions and also their stability towards oxidation under uncatalysed conditions.[201] This determines the high stability of xenobiotics (III) and (IV) in the environment. In particular the *half-decomposition time* of dioxin (I) in soil exceeds 8–10 years.[100,156,202]† The roles of photolysis on the surface[204] and of biodegradation[205] in their breakdown are insignificant. However it is necessary to consider the ability of highly chlorinated compounds (III) and (IV) with n = 7 and 8 to be converted photolytically on a soil surface into dioxin (I) and other xenobiotics with a lateral 2,3,7,8 disposition of chlorine atoms.[206] Their ability towards hydrolysis and nucleophilic substitution in strongly alkaline alcoholic solutions on heating is also known and may seriously distort analytical data.[207]

The irreversible thermal breakdown of organochlorine xenobiotics considered above occurs at temperatures somewhat exceeding 750 °C.[208] It was shown subsequently[209] that the thermal decomposition of xenobiotics (III) and (IV) is a reversible process at temperatures up to 1200 °C. Only maintaining the xenobiotics for 4–7 sec at a temperature of 1200 °C and above led to irreversible fragmentation. This circumstance produces specific requirements for the mode of operating incinerators (INC).[65] The organobromine xenobiotics (V) and (VI) are also thermally stable. Their formation and not their destruction occurs more effectively at 800 °C.[210] At the same time organochlorine xenobiotics and their organobromine analogues are comparatively readily decomposed in actual solution by UV irradiation.[211–214] Other means of non-thermal decomposition of xenobiotics are known.[211]

At the present time many of the 210 organochlorine compounds of the (III) and (IV) types of xenobiotics have been synthesised, isolated pure and studied.[198,215–220] The *danger* of such work for personnel has been reported[118] as has the need to observe the most strict precautions when working with these substances.[219] Recently there have been reports of the synthesis and investigation of a series of organobromine compounds of the (V) and (VI) type,[126–129,221] of mixed organochlorobromo compounds of the (VII) and (VIII) types,[126,127,130,131] and also of organohalo-xanthenes, xanthones and biphenyls (IX)–(XI).[132,222] The synthesis of analytically important compounds enriched with particular isotopes has been carried out.[223,224]

The *physicochemical investigation* of xenobiotics (III) and (IV) is accompanied by significant difficulties caused both by the diversity of their homology and isomeric composition and by the high toxicity of many of them. None the less fairly similar chromatographic and mass spectrometric data have been obtained for many individual isomers which is particularly important when organising their practical determination in various objects.[217–219,225–227] Spectroscopic investigations of these compounds have also been carried out in radiofrequency[216,218,220,228–231] and optical[215,232,233] ranges.

^{1}H NMR spectra have been described for many isomers of (III) and (IV)[218,220,228–230] and ^{13}C NMR spectra of certain isomers,[216] ^{1}H and ^{13}C relaxation times have been measured for individual isomers.[230,231] The possibility has been noted of using ^{1}H NMR spectroscopy in the identification and determination of individual isomers of (III) and (IV) in mixtures of them at the microgram level.[228–230] It must be stressed that ^{13}C NMR spectroscopy is an uncommon physical method of investigation, which allows spectra of previously unstudied substances to be predicted using already investigated substances as examples. A successful example of such type has been demonstrated[234] in which calculation of the ^{13}C NMR spectra was carried out for 69 isomers of the (III) series, including all those highly toxic, on the basis of known spectral data on 6 nontoxic isomers.[216]

When determining the *spatial structure* of dioxins (III) by diffraction methods it was found that the 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin molecule (the source of the known epidemic in the broiler industry of the USA[123]) is non-planar (the angle between the two faces about the O–O axis is 4.8°).[235] The structure of 2,8-dichlorodibenzo-*p*-dioxin was analogous but the molecules of 2,7-dichloro-, 2,3,7,8-tetrachloro- and octachlorodibenzo-*p*-dioxin proved to be practically planar.[236] It should be mentioned that the actual planarity of the molecule (together with the lateral disposition of the halogen atoms in the aromatic rings) is one of the key properties determining the high toxicity of xenobiotics (III) and (IV).[237] It is also interesting that in the compound (III) series the C–Cl bond length is progressively reduced with an increase in the number of chlorine atoms in the molecule.[236]

III. Sources

The known data on the sources and routes of formation of xenobiotics (III)–(VIII) have been published in a series of reviews.[48,56,58,59,61,238] Several mechanisms have been considered for the generation of these xenobiotics in relation to structure, properties of precursors and conditions of conversion. These may be nucleophilic substitution reactions, radical processes and pyrolysis. In addition an increase in the number of halogen atoms in preformed tricylic compounds occurs by electrophilic substitution of hydrogen by halogen.[58]

Sources of the xenobiotics under consideration have an exclusively *technogenic character*[239,240] although attempts are known to explain their appearance in the biosphere by forest and steppe fires.[241] The appearance of the xenobiotics in the environment beginning in the

† The half-decomposition time of dioxin (I) in soil has been reliably established for many years.[23,50] An outside report appeared more recently indicating it was from 0.5 to 1 year.[203] In the USA a similar sort of error had far reaching consequences. After inadvertent contamination of many parts of the state of Missouri in 1971–1972 by effluent from hexachlorophene manufacture containing significant admixture of dioxin (I) and the disclosure of this happening in 1974, decontamination of the territory was not carried out for many years in the hope of natural decomposition of dioxin in the soil. Only at the beginning of the eighties when it was revealed that the half-decomposition time of (I) was not 0.5 to 1 year but approximately 10 years did massive operations begin on the destruction of the consequences of the accident, including destroying the dioxin in dumps. This proved to be even more difficult to accomplish and incomparably more expensive.[67,70,71]

1940's was caused by the development of various technologies linked chiefly with the manufacture and use of organochlorine compounds. In any case proof has not been found of the accumulation of these xenobiotics in bottom sediments of rivers and lakes formed prior to 1940, i.e. before the beginning of manufacture of herbicides based on chlorophenoxyacetic acids.[239] The sources of xenobiotics (III)–(VIII) are subdivided according to economic-territorial criteria into local and diffuse (spatially distributed) and, according to the rate of accumulation in the environment and in living matter, into continuous or periodic.

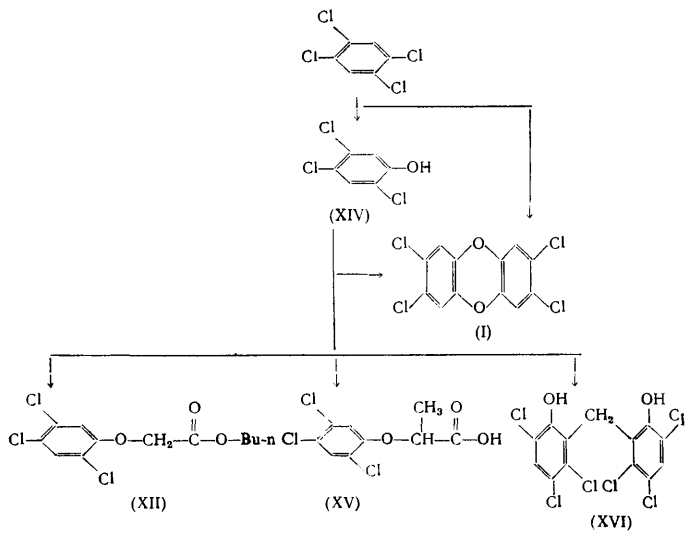
Sources delivering xenobiotics (III)–(VIII) into the environment are divided chiefly into three groups.[63,238]

1) The operation of defective manufacturing technology and the application of chemical production (of aromatic and aliphatic organochlorine and -bromine compounds, inorganic chlorides, any chemical products with the intermediate use of chlorine, inorganic chlorides, organochlorine and -bromine compounds, including use as catalysts and solvents), which are characterised by a) the presence of waste water and effluent of such manufacture,[242] b) premeditated introduction into nature of chemical products containing admixture of xenobiotics or their precursors and c) imperfect safety measures when burying or recovering effluent of chemical manufacture containing admixture of (III)–(IV).

2) Discharges from undertakings of any type (cellulose-paper, metallurgical, etc. and also undertakings specialising in the combustion of industrial and domestic refuse).

3) Automobile exhausts.

The most toxic xenobiotic (I) is formed in the manufacture of the phenoxy herbicides 2,4,5-T (XII) and Silvex 2,4,5-TP (XV), which are widely used in agriculture, and also of the antibacterial preparation hexachlorophene (XVI). Dioxin (I) arises as a side product under the actual conditions of manufacture of 2,4,5-trichlorophenol (XIV) which is the precursor of compounds (XII), (XV) and (XVI) [for example when the process is conducted at a temperature exceeding that (180°) required by the technological regulations[8,79,124]].



The content of dioxin (I) in 2,4,5-trichlorophenol (XIV) may reach 6.2 p.p.m depending on the special features of the technology‡.[243] In such final products as herbicides (XII) and (XV), the content of (I) proved to be subtantially greater [prior to 1970 the amount of (I) in products (XII) and (XV) reached 30 and even 100 p.p.m., later it was reduced to 0.01 p.p.m.[8,68]]. Considering that the greatest volume of production of 2,4,5-T occurred in 1960–1970 (its output during this period was 48.6 thousand tons) this means that the maximum quantity of dioxin (I) which was manufactured during this time may have reached 4800 kg. Significant quantities of hexa-, hepta- and octachlorodibenzo-*p*-dioxins (up to 1000 p.p.m.) have been detected in tri- and tetrachlorophenols[243] and in pentachlorophenol, widely used as a wood preservative.[243,244] In particular in the USA, the largest manufacturer of pentachlorophenol, several tons of xenobiotics (III) and (IV) were in fact 'discharged' in 1972–1977.[68]

Xenobiotics (III) and (IV) are formed in significant amounts in the *cellulose–paper industry* at the stage of bleaching the pulp with chlorine and compounds containing it.[56,133,144,245–251] This source of contamination of the environment with xenobiotics (III) and (IV) was first considered even in 1974.[245] However only investigations of recent years showed that xenobiotics are present not only in finished timber products[250] and in paper (at the p.p.t. level),[247] but also in all the technological chain, viz. the pulp itself, filtrate, the filtered off mass,[248–250] and in the solid and liquid effluent (up to 400 p.p.t.)[133,249] and the gases discharged from combustion. Up to 22 different isomers of (III) and (IV) were detected in the waste products from the cellulose–paper industry. These had 4 to 8 chlorine atoms and included 12 which are particularly toxic. The most toxic dioxin (I) was present in these mixtures in appreciable amounts.[248] Increased concentrations of xenobiotics (III) and (IV) were also found in fish, crabs and other representatives of aquafauna, inhabiting the vicinity of the drains of these undertakings.[133,249]

Incinerators (INC), which are widely used in industrially developed nations for the destruction of domestic and nontoxic industrial waste, and equipment for the destruction of toxic waste and effluent, are a steady source of xenobiotics (III) and (IV) and related substances. The first INC for the destruction of domestic waste was built in England in 1876 and at present such equipment operates for various purposes, including energy production, in great numbers in Western Europe, North America and Japan. The volumes of waste destroyed are very large. Japan burns 50 million tons waste in a year, the USA 28 million (7% total volume), FRG 8 million, Sweden 7 million, etc. Only in Canada is relatively little waste burned, viz. 1–2 million tons (in comparison it is reported that in Paris alone up to 3 million tons is burned in a year).[22]

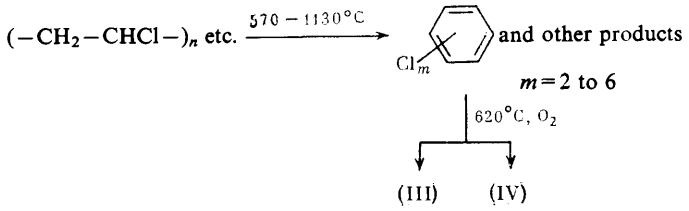
Microadmixture of (III) was found in 1977 for the first time in light ashes and effluent gases from INC in the Netherlands.[252] Later an analogous admixture was detected and studied in discharges from INC in other industrially developed countries, viz. USA and Canada,[52,253–257] England,[258,259] Switzerland and Sweden,[260–264] Italy,[265–268] FRG,[269–271] France,[272] Belgium,[273] Japan,[274–279] Austria,[279] Denmark,[280,281] Norway[282] and other countries.[51,283,284]

One INC of average productive capacity (50–200 thousand tons per year) emits 1–100 ng m^{-3} or 1–100 g xenobiotics (III) and (IV)

‡ Here and subsequently the units of measurement used will be those taken in analytical chemistry for trace amounts of organic substances, viz. p.p.m. (μg g^{-1}, mg kg^{-1}), p.p.b. (ng g^{-1}, μg kg^{-1}), p.p.t (pg g^{-1}, ng kg^{-1}), p.p.q (fg g^{-1}, pg kg^{-1}).

per year in comparable concentrations.[56,142] The amount of xenobiotics formed on burning depends on the mode of burning and the character of the refuse being destroyed. However on the whole none of the existing technologies for burning refuse is capable of preventing their formation.[48,51,63,239–240,274] Installations for destroying industrial refuse do not differ from INC in this respect.[261] Usually the attention of investigators is centred on xenobiotics passing out with effluent gases and light ash, however their presence in furnace scale transferred to burial is no less dangerous. Scales are highly toxic discharges as a result of their high xenobiotic content and their accumulation in small sized dumps.[274]

Xenobiotics (III) and (IV) are formed in particularly large amounts when burning waste containing compounds, such as polyvinyl chloride, which contain halogen atoms.[246,259,261]



Burning of bromine-containing contaminants, which are associated with many textile and other materials in amounts up to 10–20% as fire-repellants,[285] is accompanied by the formation of organobromine xenobiotics (V) and (VI).[128,129,210,286] Mixed organochlorine-organobromine compounds (VII) and (VIII) have been detected in discharges from INC.[287,288]

Routes for the accumulation of xenobiotics (III)–(VIII) have still not been finally clarified.[58,246,289] It was considered[51,246] that they are formed when processing refuse or remained undestroyed in the process for burning refuse containing these xenobiotics in trace amounts. For example representatives of these xenobiotics, chlorophenols, have been obtained on combustion of other organic materials in the presence of inorganic chlorine compounds. At the present time one is persuaded that xenobiotics (III)–(VIII) are formed in all high temperature processes involving carbon and any chlorine compound in any valency state,[270,290] but catalysts are always found in such complex heterogeneous systems. Both metallic surfaces and the surface of light ash have proved to act in this way.[289]

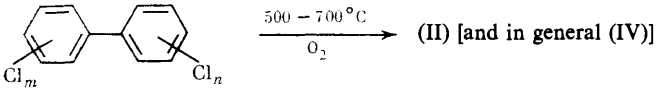
A new group of local sources has recently been revealed.[261] As it turned out xenobiotics (III) and (IV) are formed in *metallurgical plants* such as the electrochemical preparation of nickel and magnesium oxides,[291] in steel casting manufacture,[292] on smelting iron and copper scrap,[261] etc. Xenobiotics (III) and (IV) were everywhere, in waste water and discharges from these works, in the surrounding soil, in air tanks, etc.

Domestic stoves operating on coal and oil may also be local sources of the xenobiotics under consideration. The low content of (III) and (IV) in flue gases may not cause alarm[261] due to the low probability of the appearance of halogen sources in the fuel.[63] However recent data[293] showed that it is impossible to disregard this source, particularly due to its widespread distribution and uncontrolled nature.

The polychlorinated (PCB) and polybrominated biphenyls (PBB) are dangerous sources of xenobiotics of the type of (IV) and (VI). Thanks to their electrical and thermal characteristics, incombustibility and high chemical stability, these substances are widely used as liquid dielectrics and high temperature heat-transfer agents. Their worldwide manufacture exceeds 4 million tons per year.[55] Xenobiotics (IV) and (VI) are formed in the synthesis of PCB and PBB.[122,134,294] The content of (IV) in some PCB reaches 33 p.p.m.[295]

In addition xenobiotics (IV) and (VI) are also formed on overheating and burning PCB[296] and PBB.[128,137] Thus the content of compounds (IV) in rice oil contaminated with PBB proved to be two orders of magnitude greater after using it for food than in the initial PCB.[297] In conflagrations at transformer stations the concentrations of (IV) and related xenobiotics may prove to be so significant[48,59,295,298] that the restoration of damaged buildings becomes impossible.[125] In particular 8 fires in transformers containing PCB were recorded in the USA in 1981–1985 alone, including a fire at the White House in 1985. About 20 explosions and fires at capacitor installations containing PCB were known in Western European countries.[296]

The process of thermal formation of xenobiotics of the (IV) type is represented in general in the following manner.[137]



Several more detailed mechanisms of this reaction have been proposed which explain the isomeric composition of xenobiotics (IV) formed on combustion of PCB.[59]

The *exhaust gases of motor vehicles* may serve as an example of a diffuse source of xenobiotics (III)–(VI) and was described even in 1980.[241] An increase in the octane number of petrol is usually achieved by introducing dichloro- or dibromoethane or other organobromine substances together with $(C_2H_5)_4Pb$ or $(CH_3)_4Pb$. The former are precursors of harmful substances,[299] including xenobiotics (III)–(VIII).[300–303] The average output of xenobiotics by a motor vehicle using ethylated petrol is 30–540 pg km^{-1} (in dioxin equivalents, see below).[301] These amounts may be considered insignificant at first glance. The locations of heavy contamination by dioxins of motorways and regions adjacent to them are the fault of motor transport. These include poorly ventilated roadway tunnels,[142,304] soil alongside motorways with busy traffic, etc. It is also impossible to ignore the detection of xenobiotics in the exhausts of motor vehicles operating on unethylated petrol.[238]

The *water supply system* may prove to be a diffuse source of (III) and (IV). There were no communications for a long time on the detection of serious quantities of xenobiotics in drinking water after its chlorination, although the formation of (III) and (IV) in significant amounts is inevitable after introducing phenolic substances into chlorinated water after their discharge from industrial undertakings. Events which occurred in spring 1990 in Ufa, when chlorination of the water supply was obliged to be stopped due to the introduction of phenols into it by the Khimprom Industrial Combine, is direct confirmation of this.[305] It is possible

that in this case there was a direct dropping of dioxins (III) into the river and they then entered the water intake (*Arguments and Facts*, 1990, No. 33).

Industrial and other *waste products* eliminated from operations by their simple burial, storage or use may also prove to be dangerous. Such happenings were noted in Japan in places for the accumulation of large quantities of ash from INC containing (I) and (II) at 6.7 and 1.3 p.p.b. respectively.[274] Another example is the utilisation of output from PCB operations. In Japan for example after prohibition of PCB use residues (5000 tons) were burned[23] and led to the discharge of (IV). In the USA transformers and capacitors containing 600 thousand tons PCB derivatives scrapped in 1929–1977 were stored in dumps. The presence in them of only 1 p.p.b. xenobiotics implies the accumulation in the dumps of 0.6 kg dibenzofuran (II).[306] However it is known that the actual content of (IV) in PCB is significantly greater and reaches 33 p.p.m.[295]

Just how serious a problem is the storage of waste products from the manufacture of organochlorine pesticides may be judged from data of the USA,[61,307–310] FRG[311] and the Netherlands.[312–314] The quantity of dioxin (I) contained in waste products from 2,4,5-trichlorophenol (XIV) manufacture in dumps in New York state (USA) in the vicinity of Canada has been estimated at 45 kg.[61,307] In FRG in areas near Hamburg segregated for the storage of waste products from the manufacture of the herbicides 2,4,5-T (XII), Silvex (XV), lindane, etc., huge amounts (at the level of p.p.m.) of both dioxin (I) itself and many other xenobiotics (III) and (IV) were found in soil.[311] Close to Amsterdam 2000 tons organochlorine waste products, mainly from the manufacture of the herbicides 2,4,5-T and lindane, had been stored in steel drums during 1955–1970. By the beginning of the eighties the majority of the drums had disintegrated [at that time the actual waste products still contained large amounts of dioxin (I) (up to 21 p.p.m.) and (IV) isomers] and the contamination of soil layers close to the dump by dioxin (I) reached 8 p.p.b.[312,313]

The reason for the contamination of land in Missouri (USA) in 1971–1972 was the unjustified use of waste products of hexachlorophene (XVI) manufacture, which contained a large amount of dioxin (I) in vat residues. As a result in more than 40 populated localities, 5000 inhabitants proved to have been dusted with ~29 kg dioxin (from 22 to 68 kg according to different assessments). In 1974 when dioxin (I) was identified its concentration in soil in individual places reached 30 p.p.m. and even in 1983 when examination of the health of all the inhabitants living in the contaminated territory began localities were found with a contamination of up to 2.2 p.p.m.[70]

Finally the industrial manufacture of dioxin-containing herbicides itself may be converted from a local source to a diffuse source since the transportation of herbicides by the commercial route and then their spraying over agricultural or other land is practically uncontrollable. Thus the reserves of herbicides (XII) and (XV) accumulated in the USA, particularly abundant in dioxin (I), have entered many countries of the world, especially after the prohibition of their use in the USA in 1979. Several states have 'imported' dioxins from the industrially developed countries as contaminants in the herbicide 2,4-D (XIII). Although the content of the most toxic dioxin (I) in them is not large admixture of other mono-, di-, tri- and tetrachlorodibenzodioxins (III) is fairly considerable.[243]

As a consequence a huge amount of dioxin (I) and other substituted dioxins is circulating in the biosphere at present, and has been introduced over several decades together with numerous organochlorine herbicides. The herbicide 'Agent Orange' for military purposes is one of them. The average content of (I) in the latter is officially considered to be close to 2 p.p.m.§ and in previous samples (obtained from non-toxic isomers of hexachloran) it reached 47 p.p.m.[17] Overall, pesticides based on 2,4,5-trichlorophenol (XIV) are *one of the main sources of contamination of nature by dioxin (I)* and also by other less toxic but not less dangerous xenobiotics of the (III) and (IV) types.[214,315] In this context it is difficult to agree with the statement that 'the fraction of pesticides and other products of the chemical industry in the contamination of the environment is less than 5%.[64] This opinion does not rest on facts if the actual influence on the biosphere and not the volume of refuse discharged is considered.

In the middle of the eighties a first attempt was made by scientists of FRG, the Netherlands and USA at a *comparative analysis of the importance* for the active life of the biosphere of *various sources of xenobiotics* (III) and (IV).[68] This is a particularly complex problem since the known sources have differences in principle in quantitative and qualitative respects. As it turned out the considered sources may be arranged in decreasing order of danger as follows:

- –manufacture and use of the herbicide 2,4,5-T (XII),
- –pentachlorophenol,
- –tetrachlorophenol,
- –2,4,5-trichlorophenol (XIV),
- –polychlorodibenzofurans (IV) and PCB,
- –destruction of domestic refuse in INC,
- –fires in transformer installations containing PCB,
- –operations of chloro-compound manufacture,
- –combustion of chemical waste.

In conclusion it is emphasised that the available data on sources of xenobiotics (III)–(VIII) reveals only some of the most dangerous contaminated objects (or regions) with the aim of their analytical inspection for dioxin content. In future a large number of technologies will have to be studied from the point of view of the danger of generating dioxins. These will include the thermal reprocessing of carbon compounds in the presence of inorganic chlorine compounds, mild processes for the interaction of biomaterials with chlorine-containing oxidising agents, and also biotransformations of (III)–(VIII) from various products of organohalogen synthesis.

IV. Toxicity, medical effects and their consequences

After the discovery of the high acute toxicity of organochlorine xenobiotics (III) and (IV)[2–18,24,80,81,119,316] and their bromine-containing analogues (V) and (VI)[76,317] a large number of papers appeared devoted to the study of the toxicological features of these substances.[76–87,119,141,316–325] Data on the acute toxicity of

§ However some authors do not agree with the official point of view and suggest that the content of (I) in the military mixture of 'Agent Orange' was 5000 times greater than in herbicides used in agriculture. Turning in passing to the problem of the toxicity of the 'Agent Orange' mixture, which became widely known after the war in Vietnam, it should be mentioned that the presence in it of the highly toxic dioxin (I) became known to the scientific USA in 1963 and to the Presidential Scientific Consultative Committee in 1965. In 1970 the corresponding hearing took place in the US Congress after which use of the military mixture ceased.[23,148]

xenobiotics (III)–(VI) were obtained in animals and their chronic action has been studied both in animals and in man (including volunteers).[79]

Dioxin (I) possesses the maximal toxicity.[316] It is more toxic than cyanides, strychnine and curare.[326] Its toxicity is greater than, or at least comparable with, the toxicity of the antichlolinesterase poisons tabun, sarin, soman and VX gas.[326,327]

There is confirmation[91] that dioxin (I), the most toxic of substances synthesised by man, cannot in principle be regarded as a journalistic exaggeration. Dioxin is accepted as a standard for the toxicological assessment of all the xenobiotics of the (III)–(VIII) types. It must however be emphasised that the main danger of dioxin (I) and xenobiotics (III)–(VIII) in general resides in their cumulative action and the delayed consequences of chronic poisoning by extremely small doses.[49,86,93]

Table 3. Acute toxicity of some xenobiotics (III)–(VI), insecticides and toxic substances.[81,319,327–329]

Compound	LD_{50}, μg kg^{-1} (ppb)			
	guinea pig	monkey	mouse	rat
Xenobiotics (III)				
2,8-Cl_2-DD	>300 000		8 470 000	>5 000 000
2,3,7-Cl_3-DD	29 444		>3 000	>1 000 000
1,3,6,8-Cl_4-DD	>15 000 000		>2 987 000	>10 000 000
2,3,7,8-Cl_4-DD (I)	0.6–2.0	<70	114–284	22–45
1,2,3,7,8-Cl_5-DD	3.1		337.5	
1,2,3,4,7,8-Cl_6-DD	72.5			825
1,2,3,6,7,8-Cl_6-DD	70–100		1250	250
1,2,3,4,6,7,8-Cl_7-DD	>600			
Cl_8-DD			>4 000 000	>1 000 000
Xenobiotics (IV)				
2,8-Cl_2-DF			>15 000 000	>15 000 000
2,4,8-Cl_3-DF			>15 000 000	>5 000 000
2,3,7,8-Cl_4-DF	5–10	<1000	6 000	1 000
2,3,4,7,8-Cl_5-DF	<10			
2,3,4,6,7,8-Cl_6-DF	120			
Xenobiotics (V)				
2,3,7,8-Br_4-DD				⩽1000
Xenobiotics (VI)				
2,3,7,8-Br_4-DF	<15			
Insecticides				
DDT			200 000	300 000
Toxic substances				
Tabun		208		
Sarin		83		
Soman		156		
VX		20.1		

Information on the *acute toxicity of xenobiotics* (III)–(VI) is given in Table 3. Apart from dioxin (I), 1,2,3,7,8-Cl_5-DD possesses high toxicity. Some chlorinated derivatives of the (IV) series, particularly (II) and two of its Cl_5-isomers, viz. 1,2,3,7,8-Cl_5-DF and 2,3,4,7,8-Cl_5-DF, are also close in toxicity.[319,321] The toxicity of the xenobiotics indicated is many orders of magnitude greater than the toxicity of DDT and, which is very important, depends significantly on the species peculiarities of the experimental animals. The toxicities of the organobromine derivatives (V) and (VI) [organobromine analogues of (I) and (II)] and also 2,3,7-Br_3-DD[76,317] and of the mixed organobromine-chlorine compounds (VII) and (VIII) are just as high.[322]

The remaining compounds of types (III) and (IV) are less toxic than (I) and (II) although not all representatives of the (III) and (IV) series and even fewer of (V)–(VIII) have been studied in such detail.[81] In compounds of the (III) and (IV) series the xenobiotics containing from 4 to 6 chlorine atoms are particularly toxic while the presence of a lateral 2,3,7,8-Cl_4 fragment is an obligatory condition for high toxicity. In the organochlorine series there are 12 such isomers [5 in the (III) family and 7 in the (IV) family] but there are 568 if bromine and mixed chlorine–bromine compounds are considered.[130] On increasing or decreasing the number of halogen atoms the toxicity of compounds is sharply reduced.[81,319] However the danger of xenobiotics (III) and (IV) for man and nature is not just their acute toxicity. Almost all polyhalogenated compounds containing the 2,3,7,8-Hal_4 fragment, including the penta- and octa-substituted derivatives, are dangerous by various tests.[77–82,319]

The toxicological special features of the xenobiotics under consideration are linked primarily with their high lipophilicity and exceptional stability in the environment and in living organisms.[330] The lipophilic nature of the xenobiotics enables their accumulation in the organic phase of the biosphere and bioconcentration in living organisms. The xenobiotics accumulate efficiently in representatives of fauna, mainly in lipid tissue (approximately 90%[331]), liver, thymus and the blood-producing organs[142,151,331–335] and are eliminated very slowly (but from man they are practically not eliminated).[77,336,337] *Bioconcentration* is effected both by the food chain and by interphase transfer from other media, including air, water and soil (even in the case of their infinitesimal content in these media).[46,165,175,182–195,338] The high stability of these xenobiotics causes their extended retention in natural media and a long period for half-elimination from the organism of animals and man. Toxicokinetic investigations in recent years have shown that for man the *time for half-elimination of dioxin (I) from the organism reaches 6–7 years*[336,337] [for xenobiotics of the (IV) series it is somewhat lower at 1–2 years[339]].

In order to display high toxicity xenobiotics (III)–(VIII), in addition to hydrophobicity and high stability, must possess a high *affinity for their bioreceptor*,[24,77,82–85,317,329,340–343] which is known as the dioxin receptor[83–85,317,329] (although discussion on this problem still continues[344]). They must also have *high biological activity*, expressed as the concentration of substrate causing a 50% increase in the maximum possible cytochrome P-448 activity. All these requirements are possessed by those isomers of the (III)–(VIII) series of compounds containing four chlorine atoms in positions 2,3,7,8. These properties are expressed most clearly in (I) and homologues and analogues close to it in structure which fit into a rectangle of size 0.68 × 1.4 nm^2.

The rate of their *metabolism in vivo* shows an insignificant effect on the toxicity of (III)–(VIII). It was shown for (I) and (II) for example that the rate and direction of metabolism depend on the biological special features of the organism[162–164,195,345] and this process may lead to a less toxic substance.[346] In addition bioactivation in the organism by reductive dechlorination to more toxic substances may occur with Cl_5–Cl_8 derivatives (III).[164]

The diversity of mixtures of xenobiotics (III)–(VIII) actually existing in the environment and the non-equivalence of the toxic action of their individual components hinders assessment of the actual danger of these series to particular objects and regions. It has been proposed that the toxicity of each xenobiotic, chiefly of the (III)–(VI) series, should be cited in terms of a single standard, viz. dioxin (I).[347] For each compound there is a *toxicity coefficient* (TC) relative to dioxin which is determined either by the LD_{50} value,[348] characterising the acute toxicity, or by some more important quality [carcinogenic effect,[349] induction of aryl hydrocarbon hydroxylase (AHH),[350,351] a combination of several effects simultaneously,[352] etc.].[353–355] The TC system enables the toxicity characteristics of any actual mixture of xenobiotics to be reduced to a 'toxicity equivalent' ('*dioxin equivalent*', DE) if the content of each component has been previously determined. In other words, the toxicity of a complex mixture of xenobiotics (III) and (IV) may be expressed through the toxicity of dioxin (I), taken in an amount equivalent in toxicity (in overall dioxin units)¶.

Several TC systems have been proposed[33,347–355,359] and some of them are shown in Table 4 (see also Ref. 347). The complexity of the problem and the non-comparable nature of the initial toxicological packages do not permit the development of a single, generally acknowledged TC system. In the Scandinavian countries and the Netherlands for example a system[348] was used at one time which was proposed in 1982–1983 and revived in 1986 by one of the groups of investigators in the USA. It required the obligatory calculation of the contributions of isomers containing the 2,3,7,8-Cl_4 fragment. Other systems are known which were developed by specialists in the USA,[354] Canada,[352] Switzerland,[353] FRG,[359] by scientists in the northern countries of Europe (the NORDIC system in 1987[355]) and by others.[142,347] A TC system has been described[349] which operates with whole groups of isomers (Cl_4-, Cl_5-, Cl_6-compounds etc.) without separating individual isomers apart from the toxic. An international TC system has been proposed recently.[33] In the main the TC systems developed by various toxicological schools are fairly close (Table 4). Correspondingly assessments of the degree of contamination made using them (as DE) do not differ very much. However critical analysis of the actual approach to assessment of the relative toxicity of various xenobiotics (III)–(VIII) remains fruitful.[360]

Assessment of the degree of contamination of objects by actual mixtures of (III) and (IV) comprises two stages, an analytical and a toxicological. The analytical stage provides separate determination of each component of a mixture in the sample. The danger of the whole mixture (in DE) is assessed in the toxicological stage by summation of its components allowing for the TC of each. To sum up, the DE is found for an actual mixture of xenobiotics expressed in weight units of (I).

Turning to the *medical aspects of the problem* it is noted that the action of (I), (II) and in general any xenobiotic of the (III)–(VIII) series on a living organism (man or warm-blooded animals) is many-sided and depends significantly on the dose of poison, the means of its appearance in the organism, and the age and condition of the organism.[24] Even at insignificant concentrations they cause *suppression of the immune system* and disturb the ability of the organism to adapt to changing conditions of the environment which leads to a sharp suppression of mental and physical efficiency.[324,325] In somewhat higher concentrations they cause *mutagenic, teratogenic* (birth of child-monsters from affected parents) and *embryotoxic effects*, disturbance of the activity of the nervous system, diseases of the liver, digestive tract, etc.[2–18,24,49,86–95,361–364]

The clinical symptoms of disease by xenobiotics (III)–(VIII) are however not clearly expressed and the degree of poisoning by these xenobiotics is not always adequately marked. The appearance of the *disease chloracne* is frequently the first *symptom of heavy poisoning*[88–93,361,365] and in all cases there is porphyria (suppression of porphyrin metabolism). Rapid, progressing emaciation of those affected is observed with heavy poisoning.[24,49,93]

Table 4. Systems of toxicity coefficients of organochlorine xenobiotics of the (III) and (IV) families relative to dioxin (I).

Xenobiotic family	Isomer group	Individual isomers	Toxicity coefficient (TC) from data of						
			(Ref.348)	(Ref.354)	(Ref.353)	(Ref.349)	(Ref.355)	(Ref.33)	(Ref.359)
(III)	Cl_4	2,3,7,8-	1	1	1	1	1	1	1
		Others	—	0.01	0.01	—	—	—	1
	Cl_5	1,2,3,7,8-	1	0.5	0.1	0.2	0.5	0.5	0.1
		Others	—	0.005	0.1	—	—	—	0.1
	Cl_6	1,2,3,4,7,8-	0.03	0.04	0.1	0.04	0.1	0.1	0.1
		1,2,3,6,7,8-	0.03	0.04	0.1	0.04	0.1	0.1	0.1
		1,2,3,7,8,9-	0.03	0.04	0.1	0.04	0.1	0.1	0.1
		Others	—	0.0004	0.1	—	—	—	0.1
	Cl_7	1,2,3,4,6,7,8-	—	0.001	0.01	0.001	0.01	0.01	0.01
		Others	—	0.00001	0.01	—	—	—	0.01
	Cl_8		—	—	—	—	0.001	0.001	0.001
(IV)	Cl_4	2,3,7,8-	0.33	0.1	0.1	0.1	0.1	0.1	0.1
		Others	—	0.001	0.1	—	0	—	0.1
	Cl_5	1,2,3,7,8-	0.33	0.1	0.1	0.1	0.01	0.05	0.1
		2,3,4,7,8-	0.33	0.1	0.1	0.1	0.5	0.5	0.1
		Others	—	0.001	0.1	—	—	—	0.1
	Cl_6	1,2,3,4,7,8-	0.021	0.01	0.1	0.01	0.1	0.1	0.1
		1,2,3,6,7,8-	0.021	0.01	0.1	0.01	0.1	0.1	0.1
		2,3,4,6,7,8-	0.021	0.01	0.1	0.01	0.1	0.1	0.1
		Others	—	0.0001	0.1	—	—	—	0.1
	Cl_7	1,2,3,4,6,7,8-	—	0.001	0.1	0.001	0.01	0.01	0.01
		1,2,3,4,7,8,9-	—	0.001	0.1	0.001	0.01	0.01	0.01
		Others	—	0.00001	0.1	—	—	—	0.01
	Cl_8		—	—	—	—	0.001	0.001	0.001

The *epidemiological consequences of disease* from xenobiotics (III) and (IV) have been correlated in a comparatively detailed manner.[49,88,93,95,158,361,365–397] Data were obtained on examination of cohorts of people involved in industrial accidents and other mass afflictions (FRG,[56,365–368] USA,[147,157,369–373] Italy,[99,152,153,155,374] France,[375] England,[361,395] Japan and Taiwan,[95,120,121,376,377] the Netherlands,[378] Sweden,[379,380] Denmark,[381] Finland,[382] New Zealand,[383,384] Hungary,[385] Czechoslovakia[386–388] and USSR[389–393]) including occupational contact with substances in industry and in agriculture.[158,394–397] For example data are shown in Table 5 on only one group of affected people who were employed in the industrial manufacture of the herbicide 2,4,5-T (XII) and its

¶ The DE system assumes additivity of the toxic action of individual xenobiotics in complex mixtures.[68,356,357] In reality this is not always so and the need to consider synergy (see[68,358] for example) or antagonistic effects already mentioned[132,159–161] remains a practical problem.

Table 5. Illnesses of people linked with the industrial manufacture of 2,4,5-trichlorophenol (TCP) and herbicide 2,4,5-T (XII).

Year	Country	Industrial undertaking, place of manufacture	Manufactured product	Nature of illness	Number of victims	
					total	patients with chloracne
1949	USA	Monsanto, Nitro, Virginia	TCP	Explosion	228	121
1949	FRG	Nordlein, Westphalia	TCP	Industiral contact		17
1952–1953	FRG	Boehringer, Hamburg	TCP	Ditto		37
1952	FRG	Nordlein, Westphalia	TCP	"		60
1953	FRG	BASF, Ludwigshafen	TCP	Explosion	75	55
1954	FRG	Boehringer, Hamburg	TCP, 2,4,5-T	Industrial contact		31
1956	France	Rhone-Poulenc, Grenoble	TCP, 2,4,5-T	Explosion		17
1956	USA	Diamond Alkali Corporation, New Jersey	2,4,5-T	Industrial contact		29
1959	Italy	ISM, Saronno	TCP	Ditto		5
1961	USSR	Ufimsk Chemical Works, Ufa	TCP	Explosion		15
1963	Netherlands	Philips Dofar Amsterdam	TCP	"	141	69
1964	USA	Dow Chemicals, Midland, Michigan	2,4,5-T	Industrial contact	61	49
1965–1966	USSR	Ufimsk Chemical Works, Ufa	2,4,5-T	Ditto	166	128
1965–1968	Czechoslovakia	Spolana, Neratowice	2,4,5-T	"	80	78
1966	France	Rhone-Poulenc, Grenoble	TCP	Explosion		21
1968	England	Coalite Chemical Products, Bolsover, Derbyshire	TCP	Ditto	90	79
1970	Roumania	—	2,4,5-T	Industrial contact		25
1972–1973	Austria	Nitrogen works, Linz	2,4,5-T	Ditto		50
1972	USSR	—	TCP	"		1
1974	FRG	Bayer, Jurdingen	2,4,5-T	"		5
1976	Italy	ICMESA, Seveso	TCP	Explosion		193

technological precursor 2,4,5-trichlorophenol (XIV). Results of studies[35,37,79,88,389–393] were used. Altogether this group includes more than 1000 men having suffered from dioxin (I) in industrial incidents,[97] including at least 8 explosions†. The number of persons suffering from xenobiotics (IV) in connection with massive poisoning in Japan in 1968 and in Taiwan in 1979 exceeded 1850 and 2000 respectively.[95] A large volume of data on poisoning by dioxin (I) contained in herbicide 2,4,5-T (XII) was obtained by systematic examination of American and Australian veterans of the war in Vietnam and members of their families.[143,147–149] All these epidemiological data were obtained from observation of affected people over 10,[61,388,390,395] 15–20[143,373,377,397] and even 30[142,143,368] years after their contact with the xenobiotics and has enabled a more correct judgement to be made on the distant consequences of the effect on people by xenobiotics (III) and (IV).[87,90,93,396,397] As it turned out the symptoms of chloracne continued to be observed on average for 26 years.[394]

The epidemiological consequences of the contact of people with dioxins therefore have a *universal character*. They also occur in the USSR. This may be judged by the data on diseases linked with the manufacture of 2,4,5-trichlorophenol (XIV)[389,390] and herbicide 2,4,5-T (XII),[391–393] which occurred in our country in chemical works in Ufa within the framework of the usual dioxinogenic technology. The experimental output of 2,4,5-trichlorophenol began in 1961 and industrial output of 2,4,5-T in 1965.[393] Fifteen victims were recorded in the manufacture of 2,4,5-trichlorophenol.[389] The first examination of workers contacted in the process of 2,4,5-T manufacture was carried out shortly after its start by the Ufimsk Scientific-Research Institute for Hygiene and Occupational Diseases. Subsequently examinations became regular.[391,392] It became apparent that there were 128 persons with clearly expressed skin disease (serious forms of occupational acne in organochlorine manufacture), characteristic of groups affected in other countries, where there were similar industries, which amounted to 85% total number contacted. Apart from disease of the sebacious follicular apparatus of the skin, accompanying disease of the nervous system, liver, suppression of lipid metabolism, etc. was established.[391–393] Since reconstruction of the plant for the manufacture of herbicide 2,4,5-T from 2,4,5-trichlorophenol did not provide absolute protection for personnel from the development of serious forms of occupational acne and intoxication, the plant was reprofiled to 2,4-D in 1968.[393] Output of 2,4,5-trichlorophenol was stopped in 1987.

It should be mentioned however that there is extreme heterogeneity in the available epidemiological data and there are methodological errors in many investigations. The results obtained for the affected regions of South Vietnam must be considered to be the most objective. These were compared with the ecologically clean regions of North Vietnam. These data fortified by information on the quantitative content of (I) in human breast milk and lipid deposits of people[398] indicate the negative effects of xenobiotics (III)–(VIII) on the life span of the population, on its resistance towards various, especially viral, infections, towards the overall medical situation in the affected regions and towards the child-bearing function of the women. It may be considered that dioxins are one of the most important factors inducing deterioration of the racial stock of several human populations.[35–41]

Decisions have been made on the health and hygiene aspects of the problem of dioxins and related xenobiotics. The impact of these poisons and also the high probability of the appearance and accumulation in nature of dioxin synergists capable of enhancing

† The concentrations of dioxin (I) in vat residues, discovered when investigating the circumstances of these incidents, proved to be extremely significant. It was 2400 p.p.m. in Czechoslovakia, 2000 p.p.m. in USA (1964), 1000 p.p.m. in the Netherlands, 400 p.p.m. in England and 140 p.p.m. in Austria. For comparison it may be noted that the concentration of (I) in soil at the centre of the contaminated zone in Seveso (Italy) was 0.55 p.p.m.[79]

their toxic action,[358] has compelled the health and hygiene services of the industrially developed countries to conduct appropriate investigations. The appearance of dioxin-type xenobiotics in foodstuffs, drinking water and in the air of populated localities is recognised to be inadmissible. However to achieve this while vast quantities of these xenobiotics are circulating in the biosphere, while technology is operating and actually delivering these xenobiotics to the environment, is impossible. At present the problem of limiting the risk of affecting man and nature with dioxin (I) and related substances continues. For this purpose *standards* have been established for admissible *technogenic discharges of xenobiotics* by industry, limiting standards for their *content in the environment* and also standards for admissible '*consumption*' of these substances by *man*.[77,355,399–408]

The limiting standards for admissible weekly and daily consumption by man of dioxin and other xenobiotics of this type (WCD and DCD respectively) are expressed in so-called DE. These are in the form of the weight quantity of dioxin (I) the systematic consumption of which leads to an increase of one victim per million population. Values of WCD and DCD are determined in model experiments in animals by assessing the risk of a teratogenic or carcinogenic effect, immunosuppression, etc. Standards developed by a group of specialists in Sweden, Denmark, Norway, and Finland[355] for the risk of carcinogenicity are: DCD $\leqslant$ 5 pg kg^{-1} and WCD $\leqslant$ 35 pg kg^{-1} which means consumption of $\sim$2000–2500 pg DE in a week for a person of weight 60–70 kg. A similar standard (DCD $\leqslant$ 4 pg kg^{-1}) has been proposed in the Netherlands.[399] In Ontario (Canada) and FRG a DCD $\leqslant$ 10 pg kg^{-1} is considered admissible.[400,404] In USA sizes of DCD for various regions for the risk of carcinogenicity and immunosuppression vary from 10 to 0.1 pg kg^{-1}.[405] On the whole the standards for DCD adopted in the world vary within the limits 0.006 to 10 pg kg^{-1}.[33]

The developed standards for WCD and DCD are used to establish the limiting content of xenobiotics (III)–(VIII) in foodstuffs and in the water, soil and air of the environment. Proceeding from these standards the consumption of fish from internal reservoirs is prohibited, and the consumption of fish from individual farms and milk production from strongly affected regions is limited in some countries. According to the data of the Environmental Protection Agency (EPA) of the USA and of an international group of experts regions containing 1 p.p.b., i.e. 1 μg xenobiotic in 1 kg soil (in DE), are unsuitable for habitation by man. The concentration of xenobiotics in the land of stock farms must not exceed 10 p.p.t., i.e. 10 ng kg^{-1} soil (Netherlands).[402] In Sweden the standard for the limiting content of dioxins in effluent gas for INC under construction is 0.1 ng m^{-3} (for old furnaces a concentration of 0.5–2.0 ng m^{-3} is allowed).[401] In Italy[62] a content of 0.5 ng xenobiotics in 1 m^3 effluent gases is considered admissible, but investigators consider the requirements of the Swedish experts to be correct. In the USA the official standard of the EPA determining the content of dioxins in the air of work places is 0.13 pg m^{-3}.[403]

A general representation is given in Table 6 of the limiting admissible levels of xenobiotics (in DE) which must not be exceeded in the environment and in the surroundings of human habitation in general. This is composed from data of the Italian National Toxicological Committee.[21] More than 10 years study of the problem form the basis for these standards (after the events at Seveso in 1976). The set of standards for the maximum permitted concentration (MPC) of dioxin (I) in air, water, soil, etc. considered by the Minsitry of Health of the USSR has been mentioned[24] as a working alternative for the USSR. It is inconvenient to discuss them at present. However the tentative admissible level (TAL) for dioxin content in water has already been determined by the 'Health Rules and Standards for Preserving Water Surfaces from Contamination', of the USSR Ministry of Health No. 4630-88. This standard is extremely lenient at 0.000035 mg $litre^{-1}$. The fact that the document permits a standard such that the dioxin concentration in water in the USSR will exceed the Italian standard by a factor of 700 000 means that the official standard of the USSR Ministry of Health has no scientific basis at present. In particular it permits without punishment the dumping in only one year of more than 100 kg dioxin (I) in the Ufa river, an absurd amount when it is considered that US airmen sprayed 170 kg (I) in Vietnam in the course of 9 years ('Arguments and Facts', 1990, No. 33).

Table 6. Limiting levels of mixtures of xenobiotics (III) and (IV) permissible in the environment in Italy.[21]

Object	Type of material	Limiting permissible level
Air	Atmospheric air	0.04 pg m^{-3}
	Air in work places	0.12 pg m^{-3}
Water	Drinking, sea, ground water. Reservoir water	0.05 pg $litre^{-1}$
	Community sewer water after purification	0.5 pg $litre^{-1}$
	Community sewer water before purification	50 pg $litre^{-1}$
	Industrial waste water after purification	0.5 pg $litre^{-1}$
	Industrial vat residues	1 μg kg^{-1} (1 ppb)
Soil	Soil in agricultural regions	10 ng kg^{-1} (10 ppt)
	Non-agricultural soil	50 ppt
	Soil in industrial regions	250 ppt
Surfaces	Exterior walls of buildings	75 μg m^{-2}
	Internal walls and surfaces	25 μg m^{-2}

V. Determination of xenobiotics of the dioxin type

The determination of xenobiotics (III)–(VIII) in the environment and in biological samples is a most difficult analytical problem. This is primarily because the toxicological properties of these xenobiotics require that their detection limits in various materials should be substantially lower than those which are typical of many problems of organic analysis, including the determination of pesticides [for example less than 20 years ago the dose of dioxin (I) lethal for guinea pigs was less than the detection limit of the apparatus used for its determination[409]]. No less important is the structural diversity of both the actual substances being determined (see Table 1) and the compounds accompanying them. In other words there is a need to determine all the desired groups of xenobiotics (usually this is tens of substances simultaneously) the individual isomers of which differ principally in toxicity (see Table 3).

The high toxicity of dioxin (I) demanded development and introduction into analytical practice of isomer-selective methods providing detection of picogram (10^{-12} g) and even femtogram (10^{-15} g) quantities, i.e. the determination of compounds with concentrations in the p.p.t. and p.p.q. region.[143,410–436] Data on the dynamics of the reduction of detection limits for dioxin (I) during

the last 20–25 years indicate the important progress achieved in this area. Thus the detection limit of (I) in environmental samples was 1 000 000 p.p.t. in 1965, 50 000 in 1970, 10 in 1975, 0.2 in 1980 and 0.01 p.p.t. in 1983. Similar results have been obtained in the analysis of samples of herbicide 2,4,5-T (XII). The detection limit of (XII) was 1 000 000 p.p.t. in 1965 and 1000 p.p.t. in 1985. Equally significant progress has been achieved in the selectivity of the analytical methods. In 1966 20 isomers of tetrachlorodibenzo-*p*-dioxin, including (I), were determined in environmental samples as one chromatographic signal but already in 1979 it was possible to determine the most toxic isomer, viz. 2,3,7,8-Cl_4-DD, as an individual analytical signal.[105]

Thanks to wide international collaboration many procedures for determining trace amounts of xenobiotics (III) and (IV), including the most toxic, have been devised up to the present time [less for the (V) and (VI) groups as yet[418]]. The application of highly efficient purification of xenobiotics from the multitude of background substances has been proposed and includes their extraction recovery, chromatographic separation and mass spectrometric determination. This progress was provided both by improvements in analytical possibilities by instrumental technique and by the development and standardisation of methods of sample-taking and sample-preparation.

The known analytical procedures (see reviews[86,101–114] and a multitude of papers of recent years[227,414–478]) encompass practically all the important materials, viz. soil and sludges,[100,106,150,413,414,424–427,433,437–440] gaseous media including the air, smokes and exhaust gases and dust particles transported by them, ashes and fogs,[100,410,415,418,421,423,428,435,436,441–447] water,[106,417,424,429,430,432] various surfaces,[150,442,462] industrial goods and waste[413,422,425,429,430,432,441,447,448] and biological samples of vegetable[133,411,479] and animal[151,191,413,414,416,419,420,425,449–452] origin. The choice of actual procedure depends on the problems for the investigator, whether it is necessary to identify the source of discharge of xenobiotics or whether there is a need to assess an actual situation.

Two approaches have been formulated to determine xenobiotics:[102] 1) simultaneous determination of all homologues and isomers in one fraction by enrichment of the component to be measured (separation from the matrix), 2) determination of individual isomers, particularly (I) and (II) which are the most toxic. Both approaches are used for general orientation in ecological circumstances although the first is more useful for monitoring programmes. If the target is the assessment of the dioxin danger of samples and regions then the analytical procedure must be toxicologically oriented [i.e. aimed at the determination of the 12 most toxic isomers of (III) and (IV) out of the 210] and rapid (when biological methods of determination are particularly effective).[111,351,480–484]

Knowledge of the physicochemical, structural and toxicological special features of the xenobiotics under consideration, primarily (III) and (IV), enables the formulation of *general requirements* which any method of determining them in the environment and biological specimens must satisfy.[143] The procedure must provide:

1. high sensitivity, due to the exceptional toxicity of (I) and several other compounds,
2. high selectivity, for which it is necessary to separate the xenobiotics being determined from substances accompanying them in the material the concentration of which may be several orders greater,
3. high specificity providing differentiation of the desired substances within the limits of close mixtures of isomers, particularly the separate determination of the most toxic dioxin (I) in the presence of the remaining 21 Cl_4-isomers of dioxin, etc.,
4. high reproducibility of results on quantitative determination.

The first, second and fourth requirements are provided in a completely satisfactory manner by high resolution mass spectrometry. Differentiation of individual isomers in mixtures is achieved by high resolution gas chromatography.

At the present time only a limited number of analytical laboratories in the industrially developed nations are able to carry out analyses on xenobiotics (III) and (IV) of any degree of complexity, particularly to effect quantitative determination in samples of different types. The short account given below of the state of the analytical side of the problem rests mainly on the experiments of several groups working particularly effectively. They are in laboratories in Sweden and Switzerland,[102,109] USA,[101,103–105,412,413,416,441,458] Italy,[100,106] FRG,[107,108,463,464,466] Canada,[110,439,440,465] Japan,[448] France,[434] Norway[415] and other countries by whose efforts an entire methodology of determining dioxin (I) and related compounds in any sample has been built up.

Several obligatory stages are included in all the various procedures for determining xenobiotics (III) and (IV). These are the taking and preparation of samples, the isolation of the desired substances from the sample, their purification and concentration and finally the correct qualitative and quantitative determination of xenobiotics.

Techniques for *selecting a sample* must be suitable for the character of the specimen. This may be the selection of soil in a volume of fixed dimensions, selection of layers of sludge from two reservoirs, the selection and cutting of vegetables, the collection of atmospheric dust in special containers and large capacity test-samplers, wipes of dust or scraping of the upper layer of solid surfaces, the absorption of substances from water, the taking of test samples of ground or surface water and, finally, the specialised selection of biological specimens of animal origin (selection of fluids, organs and tissues). The *preparation of samples* also includes several operations, viz. sifting (soils), drying (soils and sludges), lyophilisation (biological substrates) and acid treatment (water, soils, sludges) and alkaline treatment (vegetation, residues, biological substrates).[106]

When selecting samples the problem of the amount required arises since the detection limit of the desired group of substances must be provided at the p.p.t. level and at the same time the possibility of erroneous results appearing must be avoided. In principle a detection limit of 1–10 p.p.t. of dioxin (I) may be successfully reached with a test sample of 1 g. This is particularly important for biological samples of animal origin, such as blood, milk, lipid tissue, etc. Otherwise one is obliged to deal not only with large amounts of sample but also with the hazard of the large effect of the matrix. The problem of volume is less pressing for samples of air, water and soil (discounting the role of the matrix). For the detection of femtogram quantities of (I) in air it is possible, for example, to take a sample from a volume of 1000 m^3.[415]

Recovery of xenobiotics and their subsequent purification is carried out in such a manner that the substances being determined are not lost in this process and not formed anew. This is provided by introducing into the test sample one or several internal standards from a number of compounds of types (III) and (IV) labelled with ^{13}C, ^{14}C, ^{3}H or ^{37}Cl.[106,141–143,413,485,486]

The mixture of xenobiotics is *recovered* from a sample, as a rule, by extraction with an organic solvent such as hexane, benzene, toluene, chloroform, dichloromethane, petroleum ether, etc. or solvent mixtures (hexane/acetone, chloroform/methanol, dichloromethane/cyclohexane etc.). Dimethyl sulphoxide has proved to be very effective.[425] Extraction is carried out with manual or mechanical shaking (suitable for substrates of all types) or in a Soxhlet apparatus (soil particles and air dust). The degree of recovery of the standard is usually 70–80%.[429] The more firmly the desired xenobiotic is bound to the matrix the worse is the recovery. The action of ultrasonic vibration on the sample (soil, water sludges),[106,487] absorption on polymeric resins (water, air)[106,417,423] and extraction using supercritical liquids[440] are used to increase the completeness of recovery of xenobiotics.

Various methods are used for the *purification of extracts* such as redistribution from one solvent system to another, and multistage purification using chromatographic techniques (columns, gel chromatography, high performance liquid chromatography, HPLC, etc.). The procedure for the purification of environmental samples calls for multiple chromatography (on pure silica, silica modified with sulphuric acid and on alumina), which provides recovery of all substances of types (III) and (IV) at a content of (I) at the level of 1–10 p.p.t.[100,141] Purification of biological and environmental samples is more effective using chromatography on activated carbon,[413,485] which preferentially retains planar polynuclear hydrocarbons. The effectiveness of the specific recovery of the latter by activated carbon is confirmed by comparison of the various methods of purifying (I) (on determining its content in fish)[486] and the other xenobiotics (III) and (IV).[103] Extracts of lipid tissue or samples of animal or vegetable origin are purified from readily decomposing organic substances by treatment with concentrated sulphuric acid. Generally the total process for purifying samples includes at least six procedures. These are purification on a column of the extrelut type (biological substrates), on silica gel (samples of soil and plants), on a column of Florisil (majority of substrates), on a column of aluminium oxide (majority of substrates), treatment with acid (majority of substrates) and with acetonitrile (samples with a high fat and oil content).[106]

When purifying extracts by a chromatographic technique their *concentration* and preliminary separation is effected simultaneously.

Analysis of a sample includes the determination in the purified extract of individual groups of xenobiotics (III) and (IV) (for example all 2,3,7,8-Cl_4-containing homologues and isomers, all Cl_4-isomers of DD or DF, all groups of isomers of Cl_4-, Cl_5- and Cl_6-DD, etc.) or the separate determination of each component of a mixture, especially the most toxic. This is achieved by the sequential use of chromatography and quantitative mass spectrometry, including high resolution. Occasionally their direct combination is used, for example by connecting the chromatographic column directly to the ion source of the mass spectrometer. Depending on the combination taken and the frequently fairly complex procedure each stage of the analysis (sample preparation, its introduction into the mass spectrometer, and finally the mass spectrometric determination proper) may be assigned to virtually one of three classes, viz. low, medium and high resolution. Correspondingly it is possible to effect in practice a very large number of independent procedures each of which provides resolution of an actual problem.[105]

High resolution chromatography is used for the *separation of individual isomers in mixtures*.[143] Separation of xenobiotics is carried out by temperature programming on capillary columns, prepared from glass or fused quartz, of length up to 60 m (internal diameter of the order of 0.25 mm). Silar 10C, OV-17 and OV-101, DB-5 or DB-225, SP-2330, SP-2331 and SP-2340, SE-54, CP Sil 88, SILOV, etc., are used as stationary phases.

A quadrupole mass spectrometer is used in the gas chromatographic-mass spectrometric determination of xenobiotics. Ionisation may be effected by two means, by electron impact (EI) and chemical ionisation. Ionisation by EI (ionisation conditions are up to 70 eV, 250 °C) is most suitable for Cl_4-derivatives of (III) and (IV).[137] The detection limits of 1–10 pg for Cl_4-xenobiotics (III) and (IV) and 10–50 pg for Cl_8-compounds are achieved using single and multi-ion detectors (SID and MID). To obtain a complete mass spectrum 0.1–1 ng substance is required.[109] Negative ion chemical ionisation (NCI) using methane as reagent (0.35 Torr, 180 °C) provides high sensitivity of determination of all furans (IV) with $x + y = 4$ to 8 and also of dioxins (III) with $x + y \geqslant 5$ [i.e. highly chlorinated dioxins except for (I)]. The sensitivity of this method using SID detection is 10–100 fg, i.e. 1–2 orders of magnitude greater than on using ionisation by EI.[143] The NCI technique using O_2 as reagent requires construction of a special ion source.

The use of high resolution mass spectrometry provides a further increase in selectivity and sensitivity. In particular at a resolution of 5000–10 000 using EI and SID techniques a sensitivity of 10–200 fg is achieved, which is improved for xenobiotics (III) and (IV) with the progressive transition from tetra- to octachloro derivatives.[109]

A mass spectrometric detector (mass fragmentography) is used for the *quantitative* mass spectrometric *determination* of xenobiotics (III) and (IV). The precision of determination is provided using isotopically labelled standards. This is particularly important in cases when the concentration of the desired substances in the sample is at the p.p.t. level or below.

A principal step in the determination of xenobiotics (III) and (IV) is the creation of *isomer-specific* methods of identifying and quantitatively determining individual isomers in mixtures.[102,143,216,225,276,298,448,463,465,467] The mass spectrometric method does not provide determination of individual isomers [the spectra of the majority of isomers in each of the mixtures of compounds of both types (III) and (IV) proved to be similar]. The need to determine individual isomers is dictated by the principal differences in toxicity of the individual xenobiotics forming the large series of isomers.

The possibility of separating individual isomers, such as the most toxic, is provided by a combination of high resolution gas chromatography with subsequent mass spectrometry for the quantitative determination of the separated isomers. High resolution GLC with a glass capillary column of Silar 10C (cyanosiloxane phase) is used for the separation of the most toxic isomer (I) from the remaining 21 Cl_4-DD isomers.[225] The separation of toxic dibenzofuran (II) from the remaining 37 Cl_4-DF isomers is achieved by several procedures, including capillary GC with a smectic liquid crystalline phase.[463,464] A procedure has been described for the identification of individual dioxin isomers (III) [in each of the series of (III) with $x + y = 4$ to 8] with Silar 10C[225] and SP-2330[298] columns and with activated alumina.[467] A method of identifying each of the 38 isomers of Cl_4-DF in mixtures of them has been described and was achieved using capillary columns of SP-2330 and SE-54.[217] Separation of the majority of isomers in mixtures of Cl_4-, Cl_5- and Cl_6-DF using SP-2330 columns has been reported.[298] This is particularly important when it is necessary to separate such pairs of isomers as the toxic 1,2,3,7,8-Cl_5-DF and the less toxic 1,2,3,4,8-Cl_5-DF and also the toxic 1,2,3,4,7,8-Cl_6-DF and the less toxic 1,2,3,4,7,9-Cl_6-DF which are usually eluted unseparated. Such a separation was achieved on OV-17 and DV-5 columns.[143]

The use of high resolution techniques is obligatory if xenobiotics (III) and (IV) are present in a sample at the background level. It has been shown in practice that at such low concentrations erroneous results may arise and to exclude this it is necessary to apply different methods simultaneously.[105]

Table 7. Limits of detection of dioxin (I) in various samples taken in the Seveso region.[106]

Sample type	Sensitivity, ppt	Chromatographic and mass spectrometric technique for determination
Water	≤0.01	Standard or high resolution
Air dust	60–200	High resolution
Vegetation	≤1	Ditto
Biological media	<100	"
Soil	≤1	"
Sludges	<100	Standard or high resolution
Solid surfaces	<10 ng m^{-2}	Ditto

Some successes in the determination of xenobiotics achieved in the last 10–15 years are reflected in Table 7. The detection limits of dioxin (I) given in it were obtained using standard analytical techniques when investigating samples selected in the Seveso (Italy) region after the accident in 1976.[106] Numerous correlations of that type pertaining to the whole range of possible analytical problems in the determination of xenobiotics (III)–(VIII) have been collated.[104,105]

There are definite differences in the set of procedures for determining (III)–(VI) in natural samples associated mainly with sample selection, sample preparation and the purification of extracts.[106]

Since xenobiotics are mainly in the absorbed state in *water* bound to colloids and soil particles and to a much lesser extent in the free state, their mobility is determined by the mobility of these particles. To extract xenobiotics from water samples a mixture of saturated hydrocarbons is used such as hexane–acetone (4:1) or hexane–dichloromethane. Later, samples to be analysed were passed through an absorbent material from which the samples enriched with xenobiotic were extracted with a suitable solvent such as ethyl ether. Most frequently chromatographic filtration through a column of alumina sometimes at low pressure is used for purification. Chromatography using a column with a multilayer packing or a column of Florisil remain the standard methods of purification.

Hundreds of milligrams of sample are collected when analysing *atmospheric dust* at low dioxin (I) concentrations. This is achieved using special vessels for the passive collection of dust (for a period of the order of 30 days) or high volume samplers. Attempts have been made to use electrostatic precipitators (their drawbacks were poor reproducibility of results, dependence on atmospheric moisture, a requirement for special positioning and maintenance). At the end of sample collection atmospheric moisture absorbed incidentally was separated by filtration and analysed by the specification for the analysis of water. The solid was dried for 24 h, after which xenobiotics and accompanying substances were extracted with a hexane–acetone mixture (4:1). Particles collected on the glass fibre filter of a high volume sampler were recovered in a similar manner. The extract was purified on a multilayer column and a column of alumina. Dioxin (I) and related compounds were determined in the extract by GC-MS.

In the analysis of *vegetation* it is assumed that dioxin (I) settles on the surface of samples and is there in a mobile form. Consequently in the seventies dioxin was simply extracted from grass without previous treatment and subsequent purification. More recently it has become clear that xenobiotics may also pass into plants from the soil and their level in plants may be comparable or greater than the levels in the environment. Since xenobiotics are bound to internal tissues of plants more firmly than to their surfaces after settling out of the atmosphere, samples are subjected to alkaline treatment with subsequent extraction. Three stages at least are used for the purification of (I). These are filtration through a multilayer column, through a column of Florisil (magnesium silicate) and finally through a column of alumina. In some procedures these three stages are preceded by filtration through silica gel which is required to retain highly polar compounds. The use of high resolution techniques increased the selectivity of determination. The procedures devised enable (I) to be determined in various plant organs.

When determining xenobiotics in domestic and wild *animals* data are obtained not only on their content but a correlation is found with the levels of their content in the environment (bioconcentration) as well. Previous treatment of biological samples includes alkaline hydrolysis with subsequent extraction with hexane. The extract is purified through a multilayer chromatographic column and through a column of the extrelut type. Xenobiotics have been identified and quantitatively determined in many samples using the usual GC-MS technique.

The analysis of *soil* for content of dioxin (I) and related xenobiotics was initially carried out by extraction with dichloromethane without preliminary treatment. Later an additional step has been introduced, viz. treatment with sulphuric acid and chromatographic filtration on a column of alumina, then an additional filtration on a column of Florisil. Purification with acetonitrile has also been applied. Solvents or mixtures containing no dichloromethane are used for extraction, the most effective being a hexane–acetone mixture (4:1). These preliminary purification stages enable an increase in the sensitivity and selectivity of the analysis particularly when using high resolution techniques.

As a rule the content of xenobiotics in water is below the detection limit. However they are found in *sludges*, mud and finely dispersed particles. Procedures for the analysis of sludges are similar to the procedures used for the analysis of soil. Usually sludges, mud and finely dispersed particles are first treated with acid or alkali to decompose mineral components and accompanying organic substances. This increases recovery of xenobiotics from the liquid extract. An alternative route is the drying of the sample and subsequent extraction of xenobiotics from the solid substrates.

Cotton pads moistened with a hexane–acetone (4:1) mixture are used for the collection of test samples containing dioxin (I) and related compounds from smooth, hard and non-absorbent *surfaces* (pottery, glass, tiles, plastic, varnished articles of metal and wood, etc.). To establish the degree of contamination of buildings wipes are taken of the walls, floors and windows (usually from areas of 0.5 × 0.5 m^2). The outer surfaces of buildings are examined by scraping

(1–2 mm) a square of surface 0.1–0.25 m^2 of the outer layer of the wall. Xenobiotics are extracted from cotton pads and scrapings with a mixture of hexane–acetone (4:1). Purification of the extract consists of acid treatment using a multilayer column and chromatographic filtration on alumina. Occasionally a column of Florisil is applied for intermediate purification. Detection and quantitative determination of xenobiotics is carried out by GC-MS.

Turning to the *overall organisation of analyses* of xenobiotics (III)–(VIII) it must be emphasised that this work is accompanied by considerable methodological and technical difficulties. Even within the framework of already established systems, i.e. essentially running, these analyses are extremely expensive, laborious and of long duration (as a rule they occupy many days). In addition the conduct of such analyses requires the use of special premises equipped with allowance for the very stiff requirements for accident prevention.[453–455] Because of the high toxicity of xenobiotics it is necessary that analytical samples separated for such analysis are not used for other purposes. It is also necessary that specially pure solvents, reagents and materials are used. In particular when taking air samples polyurethane or Teflon-coated glass-fibre filters are required together with polyurethane stoppers.[415,435,436] Finally the scale of carrying out analyses demands the organisation of the manufacture of standards. At present methods have been developed for the synthesis of each of the 210 xenobiotics of the (III) and (IV) series.[198,215–220,223,472]

Although many of the difficulties indicated have been overcome there are still often cases when analyses of a single specimen have been completed with serious deviations. To prevent similar errors interlaboratory comparative determinations are carried regularly in the industrially developed countries which enables comparison and standardisation of procedures.[150,419–422] The so-called 'method 8290' has been proposed for the same purpose, which enables, according to the ideas of its originators, the same results to be obtained in different laboratories by standardisation of the determination procedure.[478]

Work continues on the *improvement of techniques for the determination* of xenobiotics (III)–(VIII). Two main directions are planned. The first concerns the improvement of methods known already. Special extractors are being developed enabling the practically complete recovery of xenobiotics from soil, sludges and other materials.[426,440] Analyses are optimised both in the stages of separation of xenobiotics and in their determination. In particular computerised systems have been devised for the quantitative assessment of the results of gas chromatographic-mass spectrometric determination of xenobiotics.[468–470] Work is being conducted on the design of analytical techniques adapted for direct measurements under field conditions. For example a mobile mass spectrometer has been built in FRG which enables the direct determination under field conditions of dioxin (I) (in subnanogram quantities) and certain other highly toxic substances.[477]

The second direction concerns the development of new approaches to analysis brought into existence both by the laborious nature of the determination of xenobiotics (III)–(VI) within the framework of traditional methods and by the need to obtain express information on an actual epidemiological situation. Attempts have been made to develop *biological*, particularly immune, *methods of determining* and immediately *testing samples*.[111,351,480–484] Several biological substrates capable of specific and sensitive reaction with (I) and related xenobiotics have been proposed for biotesting (chick embryos, certain blood and sheep cells, etc.). The selective absorption of (III) and (IV) from the environment by certain flora[193] (leaves[488] and fir needles[194,489]) and fauna may be used for biotesting.[490] A radioimmunoassay has been developed for determining dioxins (III) in fish (Canada).[484]

The use of monoclonal antibodies for the immunodetermination of (III) and (IV) is particularly promising.[113,114,480] A set of antibodies has been isolated which provides a specific reaction with the highly toxic tetra- and pentachlorinated xenobiotics (III) and (IV) with lateral 2,3,7,8 disposition of chlorine atoms. These antibodies do not react with substances usually present (phenols, polychlorinated biphenyls, herbicides including 2,4,5-T, etc.). The determination of xenobiotics (III) and (IV) in material of various types, such as light ashes, motor oils, vat residues, etc., leads to satisfactory results (confirmed by correlation between data of immunodetermination and of normal GC-MS). The method provides detection of 0.5 ng dioxin (I). In our opinion this direction for analysis, in spite of several limitations, may provide a sharp drop in the consumption of time and money in the determination of samples of various types and forms a basis for effective monitoring in a practicable time scale.

VI. Environmental contamination by xenobiotics of the dioxin type. Monitoring

Problems of the chemistry of dioxin (I) in the environment[74] and the general global approach to the assessment of world-wide contamination of the biosphere by xenobiotics (III)–(VIII)[75,491,492] are still only being worked out. The previous attempt to solve this problem, accomplished in the study of the global contamination of nature by organochlorine insecticides, may only be used to a small extent. Thus xenobiotics (III)–(VIII), like the highly lipophilic organochlorine insecticides, accumulate readily in the organic phase of the biosphere and are redistricted along the food chain,[142,143] i.e. efficient participation in biotransfer is common to these two types of contaminant. At the same time the special features of the physical and chemical properties and the toxicological characteristics considered above determine the singularity of other routes of transfer of (III)–(VIII) in nature. Cases are already known at present of the efficient vertical migration of dioxin (I) in the lithosphere which determines the probability of contaminating water-bearing soil layers with it. The tendency to form stable molecular complexes in the organic phase of soils leads to an unusual, depending on soil-climate features, route for the horizontal migration of compounds (III) and (IV) in the lithosphere and to the effective conduct of transfer across boundaries. In this way modelling of the behaviour of (III)–(VIII) in nature is an incomparably more complex problem than for the organochlorine pesticides. It is made many times more complex by the extreme diversity of the homologues and isomers of (III)–(VIII).

It is known that monitoring is the most effective means of establishing the real situation for the contamination of the biosphere and is the basis for developing programmes for protecting regions, objects and populations. It is classified as chemical, biological and toxicological depending on the methods used. *Chemical monitoring* is effected by chemical, chiefly instrumental, methods. It has the purpose of recording territorial changes in xenobiotic concentration with time. *Biological monitoring* is aimed at the search for possible diseases of man and living organisms in general. *Toxicological monitoring* relates to the analysis of temporary effects of affected populations.[357,493]

The methodology of studying contamination of the biosphere by xenobiotics (III)–(VIII) comprises several parallel routes of investigation.

Firstly the methods of chemical and biological monitoring enable the *accumulation of information* on the distribution of these xenobiotics between various parts of the environment. Thus in recent years xenobiotics (III) and (IV) have been detected and determined in many new specimens such as reservoir sludges,[494] air and rain water,[172] sea and fresh-water life,[495] food products,[496] human tissue,[332,333] etc. At present there are data on the composition and content of xenobiotics (III)–(VI) in practically all parts of the biosphere: in water,[165,269,497–500] in soil and sludges,[253,304,500–506] air,[172,255,304,348,415,423,435,436,494,507–509] vegetation,[479,510] fish,[484,485,495,511] organs and tissues of warm-blooded animals,[142,143,191,332,333,495,512–518] human milk,[514,519–523] foodstuffs[141, 142,496,502,511,514,524–527] and technical products.[306,447,528] Several reports have been devoted to a study of the content and routes of migration of xenobiotics (III) and (IV) in animate and inanimate nature.[53,54,137,304]

Secondly the *geographical features* of the formation and distribution of (III) and (IV) in nature are assessed by monitoring methods. As already indicated above the composition has been studied and a quantitative assessment made of the discharge of xenobiotics when operating INC in practically all industrially developed countries of the world. The same applies also to the assessment of discharges from other sources and to the study of their content in the environment of various regions of human habitation. Such investigations have been conducted in USA,[348,453,507,521,529] Canada,[352,498,524] FRG,[300,500,501,514,519,527] Japan,[497,499,506,512,513,521] England,[63,505,510,520] Italy,[100,106,153,155,156] Sweden,[301,511,530] the Netherlands,[141] France,[531] New Zealand,[303] etc. The number of scientific laboratories occupied with this problem is growing continuously and is more than one hundred at present (47 in USA, 23 in FRG, 12 in Canada, 9 in Italy, 7 in England, 5 in the Netherlands, etc.).[33]

A particular approach to making contaminated regions apparent and clarifying the extent of their contamination is based upon the use of *data on sources* of xenobiotics (III)–(VIII). For example the total quantity of chlorophenols manufactured by the industrially developed nations is known (150 000 tons annually[63]) as is the territorial disposition of manufacture and the content of xenobiotics [predominantly of the (III) type] in each of the industrial products. In particular 99 places of manufacture of 2,4,5-trichlorophenol (XIV), of its use as a raw material in pesticide production and of the burial of poisonous waste are known and 17 of them are considered to be particularly dangerous.[532] The throughput and territorial distribution of INC are also known (2000 in Japan, 47 in FRG, 25 in Sweden,[22] 45 in Denmark,[280] 22 in northern Belgium,[273] etc.). The overall dimensions of the discharge of xenobiotics by these furnaces and the typical distribution in them of the most toxic homologues and isomers are also known. Finally the levels of consumption of ethylated petrol by the motor transport of various countries, their compositions and discharge volumes of (III)–(VIII) are known.

Allowing for these sources attempts have been made to assess the total volume of discharges and contamination by xenobiotics (III) and (IV) for actual territories and also the *dynamics of contamination* as a function of various factors. Existing experimental data on the similar ratio of homologues and isomers discharged by INC in industrially developed nations of various regions (Canada, Japan, France, Norway, etc.), regardless of the dependence on combustion regimen and the composition of the materials being destroyed,[283] was used as was data on the approximate similarity of the isomer–homologue composition of the xenobiotics discharged by various sources such as INC and motor transport.[304] However such approaches are not always reliable. In particular the hypothesis of the close relationship of homologues of (III) and (IV) present in the air in molecular form and absorbed onto aerosol particles has not been confirmed.[304] It turns out that particles transported by the air absorb the highly chlorinated (less volatile) homologues to a larger extent, thus effecting a forced separation which is not always favourable toxicologically.[172] It is also difficult to judge the quantities of xenobiotics (III)–(VIII) formed from their precursors in nature. For example the direction of the photodechlorination of the weakly toxic octachlorodibenzo-*p*-dioxin on a soil surface differs markedly from model conditions in solution. In nature a portion of the isomers of tetra-, penta- and hexachlorodibenzo-*p*-dioxin is formed by fission of *peri*-chlorine atoms, i.e. accumulation of highly toxic isomers with a 2,3,7,8-tetrachloro fragment occurs, while in solution chiefly lateral chlorine atoms are lost.[206]

It is important to know the detailed characteristics of individual suppliers of xenobiotics (III) and (IV) to bring about international cooperation on the problem of monitoring dioxins, since different sources may prove to predominate in individual countries.[63] Thus contamination of the English environment arose predominantly by the yearly inflow of xenobiotics from the manufacture and use of polychlorophenols [4.5 kg xenobiotics (in DE) from a yearly manufacture of 2000 tons chlorophenols].[63] The main sources of xenobiotics (2 kg) entering the environment in the Netherlands each year are INC.[533] In Norway the annual discharge of xenobiotics in waste water by only one metallurgical undertaking was 0.5 kg.[291]

The *integration of contributions to the contamination* of the environment by various sources of (III)–(VIII) enables assessment of the overall situation in any region and exposes the most dangerous technologies. For example assessment of the discharge of xenobiotics in Sweden in 1987 appeared as follows (in DE): combustion of domestic refuse 200–300 g, discharges from metallurgical undertakings 100–200 g, motor exhausts 10–150 g, etc. (about 1 kg in all).[534] In Canada, where discharges are more significant and contributions to the integrated contamination from individual sources are reduced year by year depending on industrial politics,[63] the following data were collected in 1986 (in Ontario province,[400] in DE): by combustion of rubbish in INC and the rendering harmless of waste water 8–10 kg, other forms of combustion 20–50 kg, impurities in polychlorobiphenyl > 4 kg, trans-border transfers (from USA) 2–20 kg, etc. Similar assessments have also been carried out for all Canada.[535] One further example of the integrated approach is the assessment by Swedish scientists of the overall content of xenobiotics in the sludges of the Baltic Sea accumulated from the whole industrial history of the region (the quantity of xenobiotics was 30 kg).[534]

When assessing *products of individual technologies* as sources of xenobiotics (III)–(VIII) it is important to know whether they are only carriers or carriers and precursors of contamination in nature. The degree of danger of a product of the first series is determined by the content in it of toxic microcontamination since the products themselves are usually effectively biodegraded in nature.[326,330] At the same time the danger of potential precursors of dioxins is not just their adequate microcontamination content since some routes for their metabolism, determined by the biological activity of the medium into which they enter, may lead to additional accumulation of dioxins in nature.

For instance paper is a product used by man in his way of living and is only a carrier of xenobiotics (III)–(VIII). Xenobiotics (III)–(VIII) are found in coffee filters, wrapping paper, paper napkins, childrens' napkins, etc.[247] Domestic use of paper is inevitably accompanied by transfer of xenobiotics directly into food (coffee, milk, butter, tea, etc.) and then into the organism.[247,536–538] The use of dioxin-containing paper is particularly dangerous for childrens' napkins, sanitary tampons, handkerchiefs, etc. since skin layers and mucous membranes extract the xenobiotics from paper.

Examples of products of the second series are polychlorophenols, polychloroanilines and their numerous derivatives, including azo and azoxy derivatives, certain polychlorobiphenyls, polychlorobenzenes, hexachlorane and other products. The manufacture and use of such products is inadmissible according to the concepts of the Environmental Protection Agency of the USA. Their danger for the contamination of nature may only be established experimentally by monitoring for dioxin.

Much attention has been paid in modern investigations to the process of transfering xenobiotics (III)–(VIII) in nature and their crossing from one phase to another. It has been shown that in air[539,540] and in water[541,542] various families of high molecular composition serve as carriers of xenobiotics. The main transport media for the transfer of xenobiotics are air and water and the atmosphere provides a more effective transport of xenobiotics from sources to an accumulating medium (or object).[174,175,494,539,540] The role of soil in the long-distance transport of xenobiotics is significantly less,[204] although our knowledge of the mechanism of the interaction of xenobiotics with the soil surface and sludges is hard to call exhaustive.[541]

When considering the problem of the *global transport of xenobiotics* it is necessary to pay attention to the principal differences between the three processes by which xenobiotics (III)–(VIII) cross from one phase to another, viz. the crossing of xenobiotics from their sources of manufacture to the environment, subsequent crossing from inanimate nature to flora and fauna, and finally, their return to inanimate nature from higher organisms. In the first case practically no changes occur in the composition of mixtures of xenobiotics. The ratios of homologues and isomers characteristic of their sources are mainly retained in inanimate nature. Only small changes are possible, explained by differences in the physicochemical properties of the xenobiotics.[283,300,543]

The picture changes sharply in the second process. Representatives of flora and fauna are particulary efficient in retaining xenobiotics with a 2,3,7,8-fragment by *bioconcentration*.[141,195,513,514] Within the homologues of this type as was made clear on analysis of the tissue of people living in different regions of the world, such as USA, Canada, Europe, and Japan,[332,333] no differences were observed in the ratio of xenobiotics. Selection is regulated in absorption concentration by the number of halogen atoms (it is most effective when $n = x + y = 8$) and accumulation during bioconcentration is effected with a toxicological orientation. It is also evidently impossible to ignore the special features of individual organisms with regard to efficient absorption of different types of xenobiotics. For example it was discovered recently[491] that the grampus concentrates xenobiotics mainly of the furan series (IV) and polychlorobiphenyls but compounds (III) are found in insignificant quantities.

When carrying out the third process, i.e. in the return *crossing of xenobiotics from higher organisms to inanimate nature*, the tendency is reversed. In biodeconcentration the most toxic xenobiotics with a 2,3,7,8-fragment effectively do not emerge from living organisms or only emerge from them as a final event.[141,544]

Precisely these features ensure that human disease by dioxins effectively occurs through the *food chain*. In this case only the most dangerous xenobiotics of the (III)–(VIII) series are consumed. The non-toxic isomers, many of which possess the properties of antagonists of (I) and (II), are selected out in the biotransfer process. Hence increased attention is being paid in practically all the industrially developed nations to the problem of analysing dioxins in foodstuffs, to the problem of manufacturing ecologically pure food and to the search for new safe foods.

Turning to biological monitoring for xenobiotics in the biosphere we note once again that the main source of their entry from the environment (soil, water and air) into man and animals is the food chain. Fish and dairy cows must receive a special mention of all the known concentrators of dioxins.[141,165,174,188,191] Xenobiotics transfer from fish to man (or to animals and birds eating them[141]) directly and from cows chiefly through milk.[175] It has been established[334] for example that xenobiotics accumulate efficiently in the milk of cows (in the lipid fraction[141]) grazing close to INC and in people using this milk (accumulation occurs more than 2 orders of magnitude more efficiently than on directly inhaling air from an INC[334]). The rate of absorbing xenobiotics from the oesophagus into animals[545] and later of transfering them into milk[338] is very high. Xenobiotics enter the offspring from the mother not so much through the placenta (natural protection operates) but more through the mothers' milk[321] and then through the oesophagus.[545] In this connection the World Health Organisation has developed an international programme on the dioxin problem in human breast milk in which practically all the industrially developed nations are involved.[141,514,520]

A detailed investigation by Swedish scientists[142] and by others[519–523] of the accumulation of dioxin in breast milk has shown that the content of xenobiotics (III) and (IV) in milk correlates with their concentration in the lipid tissue of the mother though they enter the lipid tissue from food, drinking water and the air. Direct transfer of dioxins into man through the integument from contaminated water and soil is also possible. The danger of infants being affected by dioxins is determined by the extent of the contamination of nature. Thus in 1970 there was a level of 0.8–1.45 p.p.b. of xenobiotics of type (III) in the milk of nursing mothers in South Vietnam. A large quantity of dioxins (16–30 p.p.t., in DE) was found in the maternal milk of women living in industrially more developed countries such as FRG, Belgium, Japan, the Netherlands, England, etc. The highest concentrations of dioxins (up to 30 p.p.t.) were observed in the milk of women living in huge industrial centres such as Hamburg (FRG). The first data on the dioxin content of maternal milk of inhabitants of the USSR have recently become known (obtained by scientists from USA and FRG).[546]

In conclusion it must be mentioned that monitoring of dioxin xenobiotics may be both universal and thematically or territorially oriented from the point of view of organising and financing the work.

Programmes accomplished in the USA[326,547] and Sweden[530] may be considered as examples of *universal monitoring*. The programme initiated in the USA in 1975[326] specified the carrying out of a huge series of determinations of xenobiotics in various samples in all regions of the country. Many state, industrial and university laboratories were involved. In 1983 the programme grew into a 'National Dioxin Strategy' conducted according to an assignment of

the US Congress[547] in seven main directions and emerging beyond the limits of just monitoring. In Sweden beginning in 1988 it is planned to carry out a 2.5 year universal monitoring consisting of 1000 analyses of various samples for content of xenobiotics (III) and (IV) and also of PCB, PBB and polychloronaphthalenes. The programme comprises a combination of chemical and biological methods of analysis and the samples include food, air, certain sediments, paper, INC discharges and biological specimens. The first 400 analyses were completed in 1988.[530]

Monitoring for xenobiotics (III) and (IV) is laborious and expensive (the cost of each determination including sample preparation comes to \$2000–2500[453]). In 1985 the cost of monitoring for these xenobiotics in the USA exceeded \$150 million.[63] The expenditure in Canada on monitoring up to 1985 reached \$6 million.[254] Large appropriations for similar purposes have been made in FRG[242] and Japan.[275]

Programmes for thematically and regionally oriented monitoring have been carried out regularly in the industrially developed nations. Examination of soil around Seveso (Italy) after the accident in 1976 is being continued,[156] the monitoring of regions near known 'dioxin dumps' is being carried out (Netherlands,[313,314] FRG,[311,501] USA[308–310]). In recent years vast programmes have been put into operation to study soil[505] and plants[510] in various regions of England, the 'supply baskets' of Canada,[524] FRG[527] and other countries are being examined. The toxicological monitoring of groups of people having, or having had in the past, 'contact' with xenobiotics (III) and (IV) is gradually beginning (USA[17,147,157,158,515] Japan,[95,96] Vietnam,[516,523] etc.).

Although the results of these programmes are considered to be satisfactory on the whole some alarming facts have been recorded. The analysis for xenobiotic content of fish caught in various Swedish waterways had led to the conclusion that the weekly consumption of Baltic Sea codfish in individual parts of the country exceeded the value of WCD taken as acceptable.[511] The weekly consumption of dioxins through food in West Berlin was 1.3 pg kg^{-1},[527] which is greater than the standard taken to be acceptable in some countries.[33]

VII. Prevention and destruction of dioxin contamination

Large scale measures to limit anthropogenic danger caused by xenobiotics (III)–(VIII) are being put into operation by the technically developed nations. These measures are effected in three main directions.

The first concerns the *improvement of the operating technology* whereby xenobiotics are no longer generated or their discharge is reduced to safe levels. In particular work is being carried out on modernising cellulose–paper industrial undertakings in Sweden,[548] USA[251] and other countries. New technology is being introduced for bleaching cellulose pulp which is accompanied by practically no formation of xenobiotics (III) and (IV),[548] and paper free from dioxins has already begun to be produced. Especially strict control has been established for paper for children.

Programmes have actively been put into operation for restricting the discharge of xenobiotics to the environment from the numerous INC in Sweden,[549] Japan,[275,278] Canada[254,255] and other countries. The introduction of technical improvements into the process of burning waste has provided minimum formation or even complete destruction of xenobiotics. This concerns the construction particularly of new INC.[255,259,289] An economical INC has been developed enabling elimination of xenobiotic formation in the process of burning domestic refuse.[550] A procedure has been found for destroying xenobiotics by passing the exhaust gases and light ash from the INC over a catalyst. In this case destruction of dioxins occurs almost completely even at 350–450 °C.[551] Equipment is widely used to remove xenobiotics from INC discharges and includes filters[272] and electrostatic precipitators.[552,553] In addition it is considered that the cardinal solution to the problem of destroying solid domestic waste requires prohibition of processing it without separation and use of components of the rubbish as secondary raw material.

The selection and manufacture of organochlorine compounds is being modernised in chemical undertakings. In the industrially developed nations the manufacture and application of chlorinated products, which are precursors of dioxins in nature, is prohibited. This primarily concerns 2,4,5-trichlorophenol and pesticides based on it.[49,142] In any case apparently only New Zealand manufactures and uses the herbicide 2,4,5-T in agriculture.[142] Some countries have also given up 2,4-D.[23] In some countries such as Japan the use of PCB is prohibited.[23] In others it is strictly controlled, ecologically safe replacements for these products are being developed.[142] Because of the change in composition of ethylated petrol the discharge of xenobiotics (III)–(VIII) when burning it in motor vehicles is reduced.[301] Ecologically safe methods (pyrolytic and others) of destroying chorine-containing vat residues are being developed.[532]

The second direction embraces *organisational measures* providing prevention and limitation of contamination of the environment by sudden discharges of xenobiotics. For example it is forbidden to use electric power equipment with PCB in large buildings in the USA to avoid contamination by PCB in fires,[23] which took place previously.[33,125]

The third direction of work concerns the *destruction of the results of dioxin contamination of territory*, the elimination of xenobiotics from the environment and from industrial waste and burial of the latter. Seemingly the first historically was the massive work on the decontamination of the vicinity of Seveso (Italy) from dioxin (I).[100] Similar measures were taken in the state of Missouri and in several other contaminated regions of the USA.[547,554] Expensive and very careful work has been accomplished in the industrially developed countries on the destruction of previously manufactured dioxin products such as residues of the herbicide 'Agent Orange' (USA),[310] PCB (Japan),[23] etc. Necessary measures are being applied in relation to the decontamination of large dumps which proved in fact to be sources of xenobiotics (III) and (IV) (Netherlands,[313,314] USA,[547,554] etc.).

Achievements in the area of low temperature and thermal methods of dehalogenation and destruction of xenobiotics (III)–(VIII) have been summarised.[211,532,554–556] The most effective are considered to be the destruction of dioxins by catalytic oxidation and by photodestruction, after preliminary recovery from soil with solvents and sublimation in solution at 500–600 °C. Recently biological methods of decomposing dioxins have been developed. For example fungi of certain species have been isolated which are capable of decomposing xenobiotics (III) and (IV) to nontoxic products.[557] They may find use for the partial decontamination of highly dangerous vat residues if the rate of biodestruction of dioxins by these organisms can be appreciably increased. It has been shown possible to decontaminate water contaminated with dioxins by ozonisation.[558]

Numerous procedures for the decontamination of soil and of chemical industry waste products from xenobiotics are being developed in the USA.[532,554,555] Mobile equipment has been devised for the thermal treatment of soil contaminated with xenobiotics and of solid and liquid waste at temperatures up to 4500 °C. Xenobiotics are more than 99.9999% destroyed by this.[554] A drawback of this procedure is the low throughput and high energy cost so preliminary recovery and destruction of dioxins by other methods is considered expedient. The dechlorination of xenobiotics found in waste and extracted from contaminated soil in laboratory and field conditions has been worked out by melting them with ethyleneglycol, with solid KOH or other alkalis.[559,560] Burial of soil contaminated with xenobiotics in abandoned mine workings has been proposed.[554] Special clays have been proposed for the efficient recovery of highly toxic xenobiotics (III) and (IV) from industrial waste.[532,561,562] Stabilisation procedures, including consolidation of xenobiotics in industrial waste products (such as by vitrification), have been developed.[532]

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In any event the global attempt to study the problem is thriving. Some developed countries have learned from their technological errors, others have learned from abroad. Our society must not be out of the picture while experiencing a period of brisk ecologisation. First of all this must be directed towards acceptance of exhaustive measures for the exclusion of dioxins from the environment and particularly from foodstuffs. The organisation of All-Union chemical and toxicological monitoring for this technological danger and, which is very difficult, the fitting out of our existing analytical centres of various types with appropriate instruments are also important. Finally data on the content of dioxins in the discharges from all our undertakings and in their dumps must remain an obligatory element of their technological passports.[563]

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Modelling of metal complexes by the method of molecular mechanics

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ABSTRACT. The review considers various approaches to the conformational analysis of metal complexes within the framework of the method of molecular dynamics and analyses their possibilities and limitations. The limits of the applicability and usefulness of such calculations are outlined.

The bibliography includes 128 references.

Contents

I. Introduction 1093
II. Complete allowance for the deformations of the coordination polyhedron 1094
III. The "floating point" model 1096
IV. The "rigid polyhedron" model 1099
V. Characteristic features of the modelling of polynuclear complexes 1100
VI. Simplified "mechanical" and geometrical models 1101

I. Introduction

Molecular mechanics constitutes an empirical computational method in which the molecule is regarded as a system of interacting atoms. In this model, electronic ideas are involved implicitly or are absent altogether. The method is also known as the method of atom–atom potential functions, the additive model of interatomic interactions, the molecular force field method, the mechanical model of the molecule, etc.[1] We shall use the term "method of molecular mechanics" (MMM).

Molecular mechanics is one of the most powerful methods applied at the present time in the study of the steric structure of molecules and the estimation of the energies of intramolecular and intermolecular interactions and the properties associated with them. It is applied widely in organic chemistry for the solution of various structural and conformational problems, the calculation of the strain energy, thermochemical properties, and frequencies in vibrational spectra, for the prediction of the rates of chemical reactions and their stereochemical features, for the allowance of the packing effect in condensed media, etc.[2] However, the application of the MMM in the chemistry of metal complex compounds (particularly the compounds of transition metals) is significantly complicated, as a result of which the method has not so far been used very widely.

The main characteristic feature of the MMM applied to metal complexes is the necessity to model the coordination unit, because it is by no means always possible to establish *a priori* the type of coordination polyhedron for a metal with a specified atomic (ionic) radius and a specified coordination number. Here it is necessary to take into account the possibility of the occurrence of different oxidation states of the complex-forming metal and the different structural functions of the ligand.

Furthermore, like any empirical method, the MMM requires the use of a series of parameters, whose correct determination is difficult, particularly in the case of metal complexes, owing to the lack of a sufficient amount of the necessary experimental data. The problem of the selection of the initial approximations for the calculation, which is particularly important for polycyclic chelate compounds, also complicates the conformational analysis of complexes.

In this connection, in the conformational calculations for metal complexes it is necessary to introduce additional hypotheses about the structure of the coordination polyhedron, the nature of the interaction of the ligands with the metal, etc., which is the reason for the wide variety of the modifications of the MMM applied to the chemistry of coordination and organometallic compounds. The choice of a particular model is determined by the information possessed by the investigator and by the problems which he wishes to solve.

This review deals with various approaches to the conformational analysis of metal complexes within the framework of the MMM, their possibilities and limitations are analysed, and the limits of the applicability and usefulness of such calculations are outlined.

We decided not to describe in detail the MMM, its formal features and mathematical apparatus, the form of the potential functions, the technique of the calculation, etc. and also not to consider the advantages and disadvantages of the MMM compared with the experimental and other computational methods for the study of the steric structures and molecules. These questions have been dealt with in detail in numerous publications and in a series of fundamental monographs (see, for example, Refs. 2–4). Here we shall deal with the possibilities of the most "complete" or "correct" (i.e. with the minimum number of simplifications) version of the MMM. The widely used modifications of the MMM, differing mainly in the approach to the modelling of the coordination polyhedron, will be compared and the range of problems solved with their aid will be outlined. The methods for the conformational analysis of many-centre systems (cluster compounds) will be discussed separately.

We thought it desirable to consider also a series of simple mechanical models (strictly speaking not relevant to the MMM), which, on the one hand, are closely related to this method in their "ideology" and, on the other hand, may be useful in certain cases for the study of the steric structures of complex compounds.

Since the problems dealt with in this review have already been considered in a series of other reviews and monographs (see, for example, Refs. 5–7), we shall discuss mainly the results published in 1985–1988. Early studies containing descriptions of the models and

approaches used in subsequent publications as well as the necessary experimental data are an exception.

II. Complete allowance for the deformations of the coordination polyhedron

The MMM is most widely used in the study of the structures of coordination compounds: the prediction and reproduction of the geometry of the complexes, and comparison of the relative stabilities of isomers and structurally similar compounds. In certain branches of the chemistry of metal complexes, studies of this kind have already become fairly systematic. For example, the steric structures of chelate complexes of transition metals with nitrogen-containing ligands have been studied in detail. A review[8] summarises the results of structural and conformational studies of trisalkylenediamine complexes of transition metals with the aid of the MMM—this applies mainly to cobalt(III) complexes, which apparently have in general been studied most thoroughly by this method, and to chromium(III) complexes with five-, six-, and seven-membered chelate rings. The review presents data on the relative stabilities and geometries of the structural isomers and conformers of the above complexes.

An example of the uses of the MMM for the determination of the relative energy factors favouring the existence of particular isomers of complexes is provided by a study[9] of copper(II) complexes with unsubstituted, *N*-monomethyl-, and *N,N*-dimethyl-substituted (*R*)- and (*S*)-alanines. The calculation was performed in accordance with the MM2 program[10] using the parametrisation of Raos et al.[11] in terms of the approximation of the square planar configuration of copper(II). The calculation revealed that the energies of the *cis*- and *trans*-isomers of the $Cu(Ala)_2$ complex are similar and hence that there is a possibility of the presence of the *cis*-isomer in the equilibrium mixture. In complexes with mono- and di-methyl-substituted alanines, the differences between the energies of the *cis*- and *trans*-isomers increase and in the latter case the *cis*-isomers hardly occur. According to the calculation, the complexes containing ligands with the same configuration are more stable.

Similar problems were considered in a study[12] (see also Refs. 11 and 13) of copper(II) bis-*N,N*-dimethylisoleucinates CuL_2. A detailed conformational analysis of the isomers $Cu[(S)\text{-}L]_2$ and Cu[(*S*)-L][(*R*)-L] with the same *trans*-bonding of the aminoacid ligands was carried out. A characteristic of the stability of the isomer, taking into account the contributions of the possible conformations, is the quantity $<G>$†:

$$\langle G\rangle = \frac{\sum_{i=1}^{N} G_i \exp(-G_i/RT)}{\sum_{i=1}^{N} \exp(-G_i/RT)},$$

where G_i is the energy of the *i*th isomer calculated by the MMM. The authors[12] examined 16 conformers but only three of them make the dominant contribution to the quantity $<G>$ [72.4% in the case of the (*S,S*)-isomer ($<G>$ = −1.45 kJ mol^{-1}), which is consistent with experimental data,[16] although the difference between the energies of the diastereoisomers was not in fact reproduced quantitatively.

We may note that the use of the quantity $<G>$ as a characteristic of the relative stability of the complex undoubtedly leads to more correct results than the use of the energy of the steric strain of the most stable conformer frequently employed (see, for example, Timofeeva, et al.[9]) for such estimates.

The MMM can be applied also to the study of complex bioinorganic systems. For example, the possible structures of double-stranded oligonucleotides [*d*(G1−G2−C3−C4−G5−G6−C7−C8)−*d*(G9−G10−C11−C12−G13−G14−C15−C16)] and [*d*(T1−C2−T3−C4−G5−G6−T7−C8−T9−C10)−*d*(G11−A12−G13−A14−C15−C16−G17−A18−G19−A20)]‡ and their complexes with *cis*-diamminedichloroplatinum(II) (antitumour preparations) have been investigated.[17,18] The calculations were carried out by the AMBER program[19] using different force fields whose specific parameters as well as the procedures used to model the coordination polyhedron are unfortunately not indicated by the authors. In conformity with earlier data,[20,21] the addition of the *cis*-$[Pt(NH_3)_2]^{2+}$ fragment to the N atoms of two neighbouring guanosine G5−G6 fragments was considered. It was shown that platination leads to appreciable changes in the structure of the nucleotides: it disturbs the system of stacking interactions in the chain of nitrogen-containing bases, alters the conformation of the monosaccharide as well as the system of intrastrand and interstrand hydrogen bonds in the G5−G6 region, and is accompanied by the formation of a new P=O...H−N hydrogen bond involving a coordinated NH_3 molecule and the phosphate group of guanosine G5. According to the authors,[17,18] the presence of this hydrogen bond and the changes in the steric structure induced by it influence significantly the antitumour activity of platinated oligonucleotides, which in fact explains the observed[22] decrease in this activity in the series of ligands $NH_3 > NH_2R \geqslant NHR_2 \gg NR_3$.

Subsequently the same investigators showed[23] that platination of DNA can also lead to the bending of the axis of its helix. Two such "curved" structures have been investigated[23] with the aid of the MMM in relation to the decanucleotide [*d*(TCTCG*G*TCTC)−*d*(GAGACCGAGA)]§. According to the calculation, the stabilisation of both structures is caused by the appearance of yet another hydrogen bond between the second NH_3 ligand and the O atom of the guanosine G6.

The conclusion that both hydrogen bonds play a significant role in the complexes of DNA with various derivatives of diammine dichloroplatinum has been confirmed also by Hambley,[24] who investigated by the MMM the interaction of oligonucleotides with the (*R,R*)- and (*S-S*)-isomer of cyclohexylene-1,2-diammine platinum(II).

The MMM has been used[25] to elucidate the causes of the experimentally established[26,27] addition of diamminedichloroplatinum to the −A−G− sequence of nucleotides and the absence of adducts of this kind with the −G−A− nucleotides. The trinucleotides [*d*(GT*A*)−*d*(TCC)] and [*d*(GA*G*)−*d*(CTC)] were used as models of DNA and the calculations were performed using the force field specified by Weiner et al.[28]

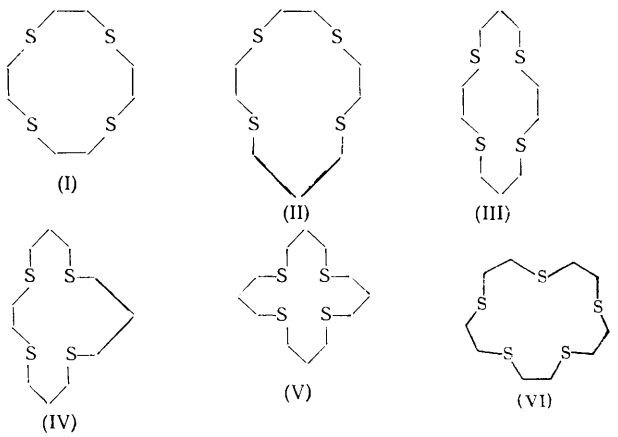
† The authors[12] refer to the quantity $<G>$ as the "Gibbs energy", although in fact it is none other than the enthalpy contribution to the steric component of the free energy of the molecule. For further details about the estimation of the latter with the aid of the MMM, see Kuz'min and co-workers.[14,15]

‡ A = adenosine, G = guanosine, T = thymidine, and C = cytidine.

§ Here and henceforth the asterisks denote the site of addition of *cis*-$[Pt(NH_3)_2]^{2+}$.

The MMM calculation showed that the formation of a complex with the second trinucleotide indicated is more favourable to the extent of 28.1 kJ mol^{-1}. This is explained by the fact that in the case of the $-A-G-$ sequence the complex is stabilised by the formation of the $-NH_3...O$ (guanosine) hydrogen bond (see above). On the other hand, in the case of the reverse sequence of nucleotides such bonding is impossible and the complex is destabilised as a result of the $-NH_3...N$ (adenosine) repulsion.

The MMM is so far used extremely rarely for the quantitative estimation of the influence of the steric factors on the reactivity of metal complexes. As one of the few available examples, one may quote a study[29] of the copper(II) complexes with the ligands (I)–(VI):

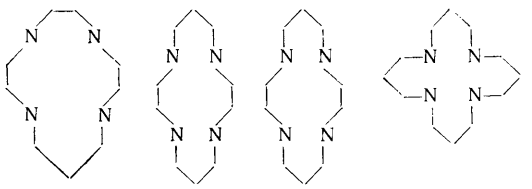


Boyd's program[30] was used for the calculations and the force field was analogous to that employed by Brubaker and Johnson.[6] The calculated structures are fully consistent with those found by X-ray diffraction (XRD).[31]

An attempt was made to subtract from the experimental[32] enthalpies and free energies of formation of the above complexes the calculated energy of the intramolecular strain in the ligands. It was found that the remaining part of the free energy, corresponding to the hypothetical complex free from intramolecular strain (ΔG_{int}), is virtually the same for complexes with the ligands (I)–(V) and amounts to 35.5 kJ mol^{-1}. At the same time, linear relations were observed between the intramolecular strain energy (ISE) calculated by the MMM and the free energy of formation of the complexes with the ligands (I)–(V) and also between the intramolecular strain energy and the logarithms of the rate constants for the dissociation of the complexes with the ligands (II)–(V) in aqueous solution.[33]

It has been concluded[29] that the enthalpies of formation of the above complexes and the enthalpies of activation for the complex formation reactions are predominantly influenced by the intramolecular strain in the ligand when the contribution of the Cu–S interactions is constant. The anomalous behaviour of the complex with the ligand (VI), which is inconsistent with the above relations, can apparently be explained, according to the authors, by the influence of the fifth Cu–S bond not only on the enthalpy components but also on the entropy components of the free energies of formation of the complexes.

The same authors investigated with the aid of the MMM the dissociation in aqueous solution of the complexes $[CoLCl_2]^+$, where L represents the nitrogen-containing macrocyclic ligands (VII)–(X) and their open-chain analogues—1,8-diamino-3,6-diazaoctane (XI) and 1,9-diamino-3,7-diazanonane (XII).



The calculations were performed using the force field of Brubaker and Johnson[6] and Boyd's program.[30]

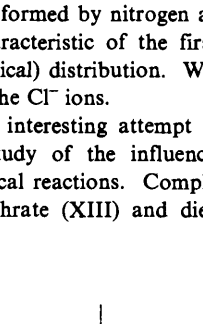
Two model intermediates formed in the hydrolysis of the complexes $[CoLCl_2]^+$ as a result of the removal of one chlorine atom from the initial molecule have been considered.[34] It was assumed that in the first intermediate the geometry of the ligand environment of the cobalt atom remains unaltered, while in the second a new geometry was calculated by means of additional optimisation. The free energy ΔG_{int} was calculated for the second model of the intermediate as had been done by Brubaker and Johnson.[29] It was found that ΔG_{int} is constant for the group of open-chain ligands (~123 kJ mol^{-1}) and the group of tetraazamacrocycles (~137 kJ mol^{-1}). The authors do not explain the difference between these quantities. In our view, the difference is caused by the entropy component of the macrocyclic effect.[35] The authors[34] also analysed in terms of the optimised structure of the intermediate the possibility of the formation of various products of the hydrolysis of the isomeric complexes of (XII).

Continuing these investigations, an attempt was made[36] to model with the aid of the MMM the first hydration shell of the complex cation $[CoLCl_2]^+$, where L is the macrocycle (VIII).

According to the model proposed by the authors,[36] the other molecules (from 1 to 14 molecules) were placed in a random fashion at distances of ~5 Å from the complex and their relative disposition was then found by direct optimisation. Potential functions without an electrostatic component were used.

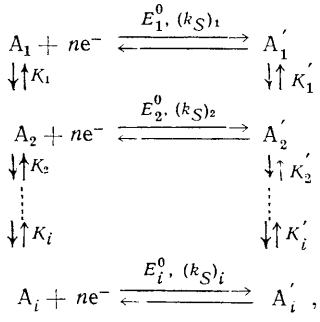
The calculations were performed for 80 different initial positions of the water molecules. The authors note that, as a result of the $-O...H-C-$ interactions, the distribution of H_2O molecules in the plane formed by nitrogen atoms outside the limits of the macrocycle is characteristic of the first hydration shell and not their random (spherical) distribution. Water molecules are more rarely distributed near the Cl^- ions.

An interesting attempt has been made[37] to apply the MMM to the study of the influence of conformational effects on electrochemical reactions. Complexes of divalent and trivalent cobalt with sepulchrate (XIII) and diethylenetriamine (XIV) were investigated.



Cobalt(III) complexes with nitrogen-containing ligands have been fairly frequently investigated by the MMM (see, for example, Brubaker and Johnson[6] and Saito[8]), but the analogous cobalt(II) complexes have been little studied. The force field proposed by Bond et al.,[37] which applies to both these and other complexes, is therefore of independent value. The results obtained reproduce satisfactorily the XRD data.[38,39]

It has been shown that the most stable conformers of complexes with divalent and trivalent cobalt are significantly different [both for the ligand (XIII) and for (XIV)] and the oxidation-reduction process is therefore accompanied by conformational transitions. Thus, according to Bond et al.,[37] the above electrochemical reaction can be represented by the following scheme:



where A_i and A'_i are conformers of complexes in different oxidation states, K_i and K'_i are the constants of the conformational equilibria, E°_i is the standard oxidation-reduction potential, and $(k_S)_i$ is the rate constant for electron transfer.

The authors compared the results of the calculation with the results of a polarographic experiment, but were unable to estimate quantitatively the nature and rates of the conformational transitions.

The calculated and experimental free energies of formation of three structural isomers of cobalt(II) and cobalt(III) complexes with the ligand (XIV) were compared. The results of the calculation did not agree with the experimental data (which is not surprising, since one is dealing with a heterogenous electrode process), but they undergo parallel changes on passing from cobalt(II) to cobalt(III).

The MMM was used similarly[40] to study the electrochemical oxidation-reduction of cobalt complexes with 1,2-propylenediamine. Four structural isomers of the above complexes were investigated. Their calculated enthalpies of formation are satisfactorily correlated with the experimental data. The oxidation-reduction potential of this system was calculated from the difference between the energies of the corresponding cobalt(III) and cobalt(II) isomers. It proved to be ~20 mV, which agrees with experimental polarographic data.

The steric factors governing the stabilities of mixed thiosemicarbazide–carboxylate complexes $CuL_n(TSC)_2$, where TSC = thiosemicarbazide and its phenyl derivatives and L = anions of monocarboxylic ($RCOO^-$, n = 2) and dicarboxylic [$R(COO^-)_2$, n = 1] acids and Cl^-, have been investigated[41] with the aid of the MMM. The calculations were performed using the CONCOORD program pack.[42]

In the series of bisthiosemicarbazide complexes (L = Cl^-), the *trans*-isomers with the diequatorial arrangement of the phenyl groups were found to be more stable. A satisfactory linear relation was observed between the conformational energies and the stability constants of the complexes in aqueous solutions. It was shown that the formation of heteroligand copper(II) thiosemicarbazide-carboxylate complexes is mainly determined by the greater or lesser steric strain in these complexes compared with the corresponding copper(II) bisthiosemicarbazide.

Thus it can be seen from the examples considered¶ that the MMM can be used successfully in the chemistry of metal complexes for the solution of different problems. It not only permits the calculations of the structures and relative stabilities of the complexes which have now come to be regarded as usual, but also it enables one to investigate their functioning and permits a quantitative estimation of the influence of steric factors on their reactivity.

However, we may note that the calculations considered above were performed for compounds with complex-forming metals which have been comparatively thoroughly investigated by the MMM [one may include among them perhaps only cobalt(III) and copper(II)], while in the case of cobalt(II) a preliminary parametrisation was required, which is impossible without an adequate set of experimental data which is difficult to obtain.

In order to perform such calculations for metal complex derivatives, various modifications of the MMM, based on the complete or partial neglect of the nature (type, dynamics) of the coordination polyhedron and on the introduction of additional *a priori* hypotheses about the specificity of the interaction of the metals with the ligands, were developed. Two models were mainly used.

The model of the first type is as follows: the form of the coordination polyhedron is not fixed, only metal–ligand bond lengths being fixed. The force constants of the L–M–L bond angles were close to zero.

In the model of the second type the coordination polyhedron is fixed and the force constants of the L–M–L angles are infinitely large.

Such assumptions naturally make the model more approximate but in many cases the use of approaches of this kind makes it possible to obtain useful information about the steric structure and properties of metal complexes.

III. The "floating point" model

An example of the most logical application of the model of the first type is the modification of the MMM, proposed by Dashevskii, Baranov, et al.,[43] which the authors called the "floating point" method or (on the basis of the mathematical procedure employed) the method of "penalty functions" (Fig. 1).

In this method, the complex forming atom is modelled by the so called "floating point".[43,44] Its interaction with the ligands is described by a penalty function of the type

$$U_{\text{pen}} = \sum_i K(l_i - l_0)^2,$$

where K is an empirical constant—the contribution of the penalty function to the overall target function (for further details, see Baranov et al.[44]), l_i is the distance from the donor atoms of the ligand to an arbitrary "floating" point with the coordinates X, Y,

¶We recall that we are dealing with the most "complete" version of the method, i.e. the calculations were performed taking into account both the deformations of the coordination unit and the non-valence L–M interactions.

and Z, and l_0 is the specified length of the coordinate bond. The summation is carried out over all the possible metal–ligand bonds and the resulting quantity U_{pen} is added to the energy of the intramolecular interactions calculated by the MMM. Next, the minimum in the overall target function is sought with respect to all the conformational parameters of the ligands and the coordinates of the point.

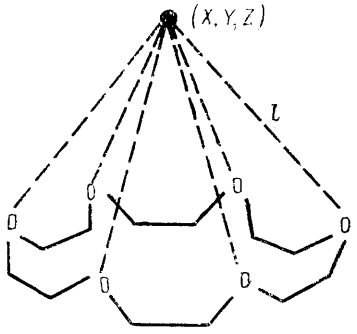


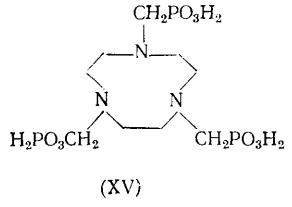
Figure 1. The "floating point" model.

By repeating calculations of this kind for variable values of l_0, one determines the $\Delta E = f(l_0)$ relation, each point of which reflects the energy expended by the ligand on the rearrangement to the conformation characteristic of it in the complex with the cation i separated from the donor atoms by a distance l_{0i}. If the above relation has a deep minimum, then the position of the latter defines the optimum length of the coordinate bond, the geometry of the coordination unit, and the conformation of the chelate rings.

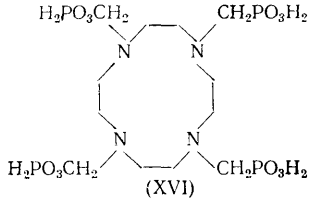
Thus in the method described account is taken only of characteristics such as the metal–donor atom bond lengths. The type of coordination polyhedron is not then fixed and non-valence interactions between the metal and the atoms of the ligand as well as the nature of the deformation of the metal–donor centre bonds are disregarded. An undoubted advantage of the method of penalty functions is the fact that the curves obtained for the variation of the conformational energy of the ligand with the length of the hypothetical coordinate bond can be interpreted in many instances as selectivity curves, using them for the analysis of the possibility of the adaptation of the given ligand to a particular metal cation.[45] We may also note that the above curves reflect to some extent not only the result but also the cause of the conformational rearrangement of the ligand during complex formation.

An example of the use of the "floating point" method may be provided by a study[44] (see also Refs. 43 and 46–48) of the complex-forming properties of tetraphenylmethylenediphosphine dioxide $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)_2$. The dependence of the conformational energy (taking into account the "penalty") of the complexes ML_3 on the metal–ligand donor atom distance was investigated in this study. It was shown how the structure of the coordination unit varies as a function of l_0: for l_0 = 3 Å, the coordination polyhedron is an almost regular octahedron with a twist-conformation of the chelate rings; for l_0 = 2.5 Å, it is a regular prism with the chelate rings in the chair conformation; for l = 2 Å, it is a distorted octahedron with two chelate rings in the boat conformation and the third one in the twisted chair conformation. It has been stated[44] that these results reproduce satisfactorily the experimental data[49,50] for the structure of the coordination polyhedron in complexes of this kind.

The method of penalty functions is usually employed to investigate the complex-forming capacity of macrocyclic polydentate ligands. Thus a theoretical conformational analysis of the macrocycles (XV) and (XVI) with exocyclic groups containing donor centres (cyclopendants) has been carried out[51] (see also another study by Kabachnik, et al.[52]).



(XV)



(XVI)

Analysis of the dependences of the conformational energy on l_0 (by a procedure similar to that described above) showed that the optimum length of the M–L bond for the ligand (XV) is 1.95 Å. The ligand is then in the hexadentate "twisted basket" conformation. The selectivity of the ligand (XV) in this conformation is significantly greater than that of (XVI) for which the most favourable lengths of the coordinate bonds are in the wide range 1.9–2.2 Å. The maximum denticity of the ligand (XVI) is not achieved. It exhibits a denticity of 5 or 6. According to the calculation, in certain cases [for example in the copper(II) complex[52]] the ligand (XV) is also in the pentadentate conformation, which indicates the possibility of a ready adjustment of the ligand contour of the cyclopendants with respect to the coordination polyhedron characteristic of the metal ion.

The results obtained agree with the experimental data[53,54] for the stability constants of the transition metal and group II metal complexes with the ligands (XV) and (XVI).

The method of penalty functions has also been used[55,56] to estimate the selectivity of the formation of crown-ether complexes. A study was made of the influence of the ring size and of the number and relative positions of the donor atoms on the capacity of macrocyclic complexones for adaptation. It was shown that both an increase in ring size and an increase in the number of donor centres increased the selectivity of macrocyclic ligands. In the first case, the length of the hypothetical coordinate bond corresponding to the optimum conformation of the complex diminishes under these conditions, while in the second it increases. The introduction of conformationally rigid fragments into the ligand diminishes its selectivity. It has been established that analysis of the selectivity curves obtained by the method of penalty functions permits a satisfactory prediction of the relative stabilities of the complexes of crown-ethers with alkali metal ions.

A model similar to the method of penalty functions, which the authors called[57,58] the "hinged model", has been used to investigate the structures of transition metal complexes $M(CO)_6$, $CpM(CO)_n$ (n = 3, 4), $(\eta^4\text{-}C_4H_6)M(CO)_3$, MCp_2, $M[C_5(CH_3)_5]_2$, Cp_2MX_2 (X = H, Cl, CO), and Cp_2MH_3. The calculations were performed in accordance with Boyd's program.[30]

In the model discussed, as in the method of penalty functions, the force constants for the deformation of the angles at the metal atom were assumed to be zero. Thus the form of the coordination polyhedron is not controlled and the ligands bound to the complex-forming agent can rotate freely around the centre ("hinge"). However, in contrast to the "floating point" model, in this modification of the MMM the M–L bond lengths are not varied and their values, taken from X-ray diffraction data, are fixed by specifying higher force constants (the analogue of the "penalty").

The optimum disposition of the ligands corresponds to the minimum in the energy of the non-valence interactions between them (as in the "points on a sphere" model[59]) and the non-valence interactions with the metal atom are not taken into account.

The calculations performed on the basis of the "hinged" model made it possible to reproduce qualitatively the relative disposition of the ligands in the structures most typical for organometallic compounds (half-sandwich, sandwich, and bent sandwich). A satisfactory agreement was achieved between the calculated and experimental ligand–metal–ligand angles (the discrepancies were 5–10°). Certain regular features observed in the structure of π-complexes were reproduced.

The "floating point" ("hinged") model described can apparently be used quite correctly to carry out calculations for complexes with isotropic spherical complex-forming metal cations (alkali and alkaline earth metals—see, for example, Trigub[55] and Kuz'min[56]). On the other hand, its application to transition metal complexes is significantly restricted (as has been justly noted by Slovokhotov, et al.[57]) to the range of compounds for which the principle of the uniform filling of the coordination sphere by the ligands holds. These include, for example, complexes in which the transition metal atom attains the 18-electron inert gas shell environment ("quasi-spherical" ligand environment[60]) and complexes in which "premature" dense filling of the coordination sphere by ligands takes place (for example, π-complexes[57]).

It is noteworthy that consideration of the legitimacy of the assumption of the elasticity of the bond angles (and hence of the applicability of the "hinged" model) is outside the framework of the MMM and should be based on experimental data or on the results obtained by more rigorous computational methods.

When applied correctly, such models, neglecting the elasticity of the bond angles and the metal atom, make it possible, as shown above, not only to estimate the conformational changes in the ligand occurring on complex formation but also to reproduce qualitatively the type of coordination polyhedron and also (using the procedure of "penalty functions") to investigate the process dynamics and the influence of steric factors on the selectivity of the complex formation.

We may note that in all the models examined above no account is taken of non-valence metal–ligand interactions, allowance for which (which naturally requires an additional parametrisation) increases significantly the reliability of the results obtained with the aid of these approaches. When no account is taken of non-valence interactions, a situation may arise, in particular, where the "floating point" coincides with one of the non-donating ligand atoms or is "superimposed" on one of the bonds (which lacks physical significance for understandable reasons).

An attempt to take into account non-valence interactions of the metal–ligand type was undertaken in a study[61] of β-diketonate (β-dik) lanthanide complexes $Ln(\beta\text{-dik})_3L$ (Ln = Eu, Yb; β-dik = acetylacetonate, dipivaloylmethanate; L = water, quinuclidine). The authors[61] consider these complexes as models for the study of the steric factors governing the functioning of lanthanide shift reagents in NMR spectroscopy. A modified[61] MM2 program[10] was used in the calculations. Here the force field was expanded by incorporating in it the force constants of the bonds and bond angles, the barriers to rotation, and the parameters of the van der Waals interactions with participation of Eu and Yb atoms (with the exception of the force constants of the bond angles at the metal atom). The calculated structures of the complexes agree well with those found by the X-ray diffraction method;[62,63] it was shown that the most favourable conformations correspond to the three-bladed propeller form.

It has been suggested[64] that not only non-bonding interactions of the metal atom (without additional parametrisation) but also the form of the coordination polyhedron be taken into account within the framework of the "floating point" model. For this purpose, the penalty function is supplemented as follows:

(1) By quasi-non-valence interactions of the "floating point" with the ligand atoms which are not donor centres, in conformity with the hard sphere approach:

$$F_{r_i^*<r_0} = \begin{cases} 0, & r_i > r_0 \\ U_{\max}, & r_i \leqslant r_0 \end{cases},$$

where r_i is the distance from the "floating point" to the ith ligand atom, r_0 the van der Waals radius of the ith atom, and $U_{\max}$ an empirical constant—the "barrier" to the collision of atoms.

(2) By quasi-elastic angular deformations:

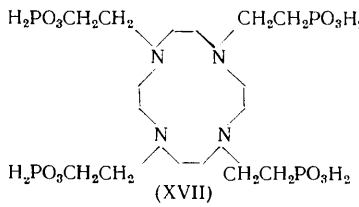
$$U_{\text{def}} = K_2 \sum_i (\alpha_i - \alpha_0)^2,$$

where K_2 is an empirical constant (the contribution of the deformation of bond angles to the overall target function), α_i are the angles formed in the ligand–"floating point"–ligand system, and α_0 are the bond angles characteristic of the donor atoms of the ligands and of the quasi-coordination polyhedron corresponding to the "floating point".

For comparison, the calculation was performed in terms of the approximation described[64] for 18-crown-6, the cryptand[2.2.2.], and the cyclopendant (XVI), which had been investigated previously[43,51] without the refinements indicated. It was shown that such correction of the penalty function influences significantly the form of the dependence of the energy of the molecule on the metal–ligand distance, particularly on the steepness of the walls of the "potential well". Some of the conformations of the ligands indicated, generated previously, proved to be artefacts.

However, one may note that the observed effects are in all probability not associated with the introduction of quasi-elastic angular deformations into the penalty functions; they depend to a large extent on the selection of the initial approximation for the conformational calculations.

Complexes with the cyclopendant (XVIII) have also been investigated:[64]



(XVII)

It was established that the ligand (XVII) [similarly to the ligand (XVI)] in the complex has a folded conformation of the macrocycle while the increase in the length of the exocyclic groups diminishes the selectivity of the complex formation with participation of the ligand (XVII).

There is no doubt that the additional features described increase the applicability of the method of penalty functions, although the "adjustable" character of the coefficients employed nevertheless reduces the correctness of this approach.

IV. The "rigid polyhedron" model

As an example of the use of the model of the second type (see above) we shall consider the approach[65–68] in which the complex-forming atom is modelled by an "ideal" polyhedron. Its configuration is specified on the basis of experimental data referring either to the complex itself or to its analogues and it does not change during the calculations (the lengths of the metal–ligand bonds and the ligand–metal–ligand angles are constant, as a result of which this approach can be referred to as the method of "rigid" or "ideal" polyhedra (the name is conventional because the authors themselves do not name their model). The non-valence interactions of the metal with the ligand atoms as well as the barriers to rotation about the metal–ligand bonds are ignored in this method.

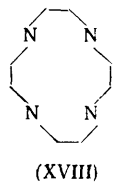
An important component of the above method is the procedure used to search for the initial approximation for the optimisation of the geometry (it is of an especially great current interest for complexes with polydentate ligands forming several chelate rings with common edges). It consists in sorting through all the possible combinations of chelate rings having different conformations taking into account the "rigidity" of the coordination polyhedron. Referring to this process as "assembly on a templet", the authors[65–68] see in it some analogy with templet synthesis. The number of combinations is limited by the steric conditions governing the cross-linking of the chelate rings. A preliminary study is made of the conformational possibilities of the isolated chelate rings and the families of the most favourable conformations and the ways in which they can undergo interconversions are found (see, for example, Pletnev and co-workers[66,69]).

This method of selecting the initial approximation has undoubted advantages—it guarantees the selection of initial approximations which are known beforehand to correspond to the topology of the coordination unit and makes it possible to monitor the configuration of the complex.

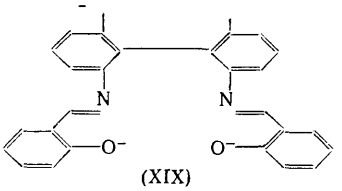
The approach described has been applied successfully to the calculation of the structures of various metal complexes using the specially developed FORCON program.[66]

Thus the structure of the cobalt(III) complex of the macrocycle (XVIII) having the composition $[CoL(NO_2)_2]^+$ with the *cis*-octahedral (with respect to the nitro-groups) coordination of cobalt has been calculated[65] (see also Pletnev, et al.[66]). The calculation yielded two structures, one of which (less favourable) agrees well with X-ray diffraction data.[70]

Pletnev, et al.[65] investigated the steric structure and the stability factors of the cobalt complex with the ligand (XIX).



(XVIII)

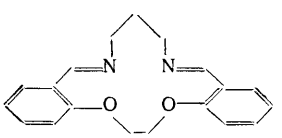


(XIX)

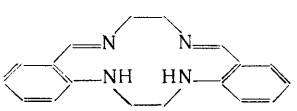
The conformational analysis of the salicylideneamine chelate ring showed that its optimum conformation is non-planar and the deformation of the bond angles is minimal. At the same time, the flattening of the ring does not require much energy expenditure (9.2 kJ mol^{-1}).

The structure of the above complex was calculated in terms of the approximation of the following coordination polyhedra: square, distorted square ("twisted" via the diagonal twist mechanism by 30°), distorted tetrahedron (square "twisted" by 67.6°, which is consistent with the experimental data[71]), and a tetrahedron. Although the results for the distorted tetrahedral structure agree well with experiment, this structure is not most favourable from the standpoint of steric strain in the ligand; the structure of the distorted square, twisted by 30°, is optimal. Evidently the occurrence in the complex of the distorted tetrahedral configuration is determined by the characteristic features of the crystal packing. The authors state that the changes in strain energy on formation of the polyhedron are comparable to the measured enthalpies of the square–tetrahedron interconversion (~20 kJ mol^{-1} [72]) and the contribution of the steric strain in the ligand to the stabilisation of a particular polyhedron should not be neglected.

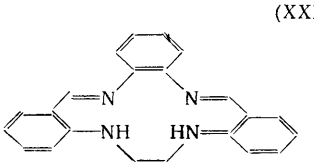
Complexes of the following macrocyclic reagents have been investigated:[67]



(XX)



(XXI)



(XXII)

Calculations have been carried out for the structures (XX)–(XXII) and the conformations the optimum (from the standpoint of the possibility of coordination) directions of the lone pairs of the donor atoms of the ligands were discovered. The following versions of the geometry of the coordination unit were considered: square, tetrahedral and distorted tetrahedral, bisphenoidal, octahedral, trigonal-bipyramidal, tetragonal-pyramidal, and linear. The formation of square and bisphenoidal complexes is not favourable for the ligand (XX), whereas tetrahedral and distorted tetrahedral complexes cannot be formed for steric reasons. The "capped" (tetragonal-pyramidal) structure of the coordination unit proved to be optimal for complexes of the monoanions of the

tetraazamacrocycles (XXI) and (XXII), while the square structure proved to be optimal for the dianions. The results obtained are in the main consistent with X-ray diffraction data.[73,74] An attempt was made to justify certain extraction properties of the reagents (XX)–(XXII) on the basis of the probable structures of the complexes.[65–68]

The nickel complexes NiL_2 [L = *o*-hydroxyazobenzene (XXIII), *o*-mercaptoazobenzene (XXIV)] with a square-planar configuration of the coordination polyhedron have been examined.[68] The calculated structures of the complexes reproduce satisfactorily the experimental data.[75] The steric factors promoting the formation of six-membered [for the ligand (XXIII)] and five-membered [for the ligand (XXIV)] chelate rings are being interpreted.

Thus the "rigid polyhedron" approach described is entirely suitable for the calculation of the structures of structurally varied metal complexes. Its undoubted advantages include allowance for the configuration of the coordination unit and the corresponding steric organisation of the donor centres of the ligands ("the locus" of the macrocycle according to the authors terminology[65,68]). The method of selecting the initial approximations is also novel.

At the same time, although the approach described takes into account the geometry of the polyhedron it does not consider other characteristics of the complex-forming atom. No account is taken of either the distortions of the coordination polyhedron under the influence of the ligand environment or of the features of the conformational behaviour of the ligands in the field of the non-valence interactions with the central atom or ion. This is probably the explanation of certain inaccuracies in the results, which have been pointed out by the authors themselves.

Furthermore, the question of the selection of a particular type of coordination polyhedron in the absence of experimental data for the structure of the complex investigated remains open. The authors[67] suggest that various ideal polyhedra should be "sorted through" with comparison of their steric strains, but this approach is also only a palliative.

V. Characteristic features of the modelling of polynuclear complexes

In our view, the attempts to apply the MMM to the study of cluster compounds merit special consideration since allowance for the specific features of the structures of polynuclear complexes involves additional difficulties.

The main problem arising in the application of the MMM to calculations for complexes of this kind consists in the fact that the method requires an unambiguous determination of the orders of the bonds involving the atoms in the molecule, because the deformation of the valence bonds and the non-bonding interactions are described in the MMM by fundamentally different potential functions. Even when X-ray diffraction data are available, in the case of clusters it is frequently impossible to determine unambiguously the metal–metal and metal–ligand bond orders.[76] To overcome these difficulties, it has been suggested,[77] for example, that the interaction of the ligands with the metallic core as a whole and not with specific metal atoms be considered. The concept of an "equipotential surface of the cluster", formed on combining (for further details, see Lauher[77]) the spheres circumscribed around each metal atom (the radii of the spheres correspond to the metal–ligand donor atom bond lengths), has been introduced. Thus the cluster core is replaced by a kind of "superatom".

In the calculation of the energy of the steric strain within the framework of the MMM, additional terms are introduced, taking into account the distance of the ligand from the equipotential surface and the deviation of the ligand axis (for example the C–O bond for carbonyls) from the direction normal to this surface. These contributions are calculated in different ways for the regions corresponding to the bridging and terminal bonding of the ligands (the subdivision of the equipotential surface is based on X-ray diffraction data).

This approach was used to study a series of metal carbonyls with the compositions $Fe_2(CO)_9$, $Co_2(CO)_8$, $Fe_2(CO)_8^{2-}$, $CoFe(CO)_8^-$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Fe_4(CO)_{13}^{2-}$, $CoFe_3(CO)_3^{2-}$, $CrFe_3(CO)_{14}^{2-}$, and $Mn_4(CO)_{16}$. The results of the calculations for these complexes (in accordance with Allinger's program[10]) agree well with X-ray diffraction data.[78–82] Furthermore, in the study of these complexes a dependence of the metal–metal bond length on the steric strain energy was noted. Another relatively simple approach was used by Newson and co-workers[83,84]—"interactive molecular graphics"—in the study of the steric structures of clusters. In this model, the dependence of the energy of the steric strain of the molecule on one or two internal coordinates (usually torsional angles) is investigated. The geometry of the remaining part of the complex is then fixed on the basis of X-ray diffraction data. The intramolecular strain energy involved only non-bonding van der Waals interactions (with the parametrisation of DelRe, et al.[85]), while the contributions of metal atoms are disregarded. Despite the evident deficiencies associated with the neglect of a number of important factors, this approach can be used in some cases to estimate steric strain.

Thus the steric hindrance in the complex $Fe_4(CO)_{12}CR$ (R = CH_2, CH_3, CO_2CH_3) caused by the presence of the substituent R was investigated[83] with the aid of the "interactive molecular graphics" (X-ray diffraction data were used[86]). In the determination of the steric hindrance in the cluster, the variable parameter is the torsional angle around the C–R bond, whose magnitude in the optimised conformation agreed with experimental data[86] to within 5°. It was shown that the steric hindrance in the cluster increases significantly when the sp^2-hybridised hydrogen atom in the substituent R is replaced by a sp^3-hybridised hydrogen atom. The dinuclear complexes $[CpMoS(\mu\text{-}S)]_2$, $[C_5(CH_3)_5MoS(\mu\text{-}S)]_2$, and $[(C_2H_4S_2)MoS(\mu\text{-}S)]_2$ were investigated similarly.[84] Scanning with respect to the Mo–S–S–Mo torsional angle revealed the stable conformations of the complex, which proved to be consistent with the experimental ones.[87] It was shown that the stability of the *anti*-isomers of the above complexes is greater than that of the *syn*-isomers.

The interaction of the iron(III) complexes $[Fe_3O(H_2O)_3Piv_6]^+$ (A) and $Fe_6O_2(OH)_2Piv_{12}$ (B) (where Piv = pivaloyl) with the hydroperoxide of dibenzyl ether has also been examined.[88] In the calculation of the steric strain energy, X-ray diffraction data were used[89,90] and the variable parameter was the Fe...O–OR distance.

H

It was shown that the lower catalytic activity of the hexanuclear complex (B) compared with the tetranuclear complex (A) in the hydroperoxide decomposition reaction may be caused by the greatest steric hindrance occurring in the coordination of the latter to the catalytic centre of the complex.

The disadvantages of the models described above include, firstly, the neglect of the metal–metal interaction and also non-bonding metal–ligand interactions and, secondly, the impossibility of carrying out calculations of this kind without X-ray diffraction data.

The approaches described do not allow calculation for the intrinsic metallic core of the cluster although they do take into account the steric effect associated with the influence of the ligand environment.

We may note, however, that even such limited information can in many instances be useful for the elucidation of the causes of the formation of polynuclear complexes with a specific structure.

An attempt to take into account the above interactions in the calculations for polynuclear metal complexes (in the absence of a metal–metal bond) has been undertaken in studies[91,92] of copper complexes of 1,2-dicarboxylic acids with the composition $Cu_2L(OH)_2.2H_2O$ {L = anion of succinic, 4-cyclohexene-1,2-dicarboxylic, 3-methyl-4-cyclohexene-1,2-dicarboxylic, 4-methyl-4-cyclohexene-1,2-dicarboxylic, and *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids}. It was shown that the complex $Cu_2L(OH)_2.2H_2O$ can be represented as a superposition of two isomeric structures with bond bidentate-cyclic and bidentate-bridged coordination of the carboxylate groups. With increase in the structural rigidity of the ligand, the contribution of the isomer with the bidentate-cyclic type of coordination increases.

The most correct method of applying the MMM to the study of cluster compounds involves undoubtedly the generation of force fields, including, among other parameters, the force constants for metal–metal bonds and the corresponding constants for the bond and torsional angles. This approach was in fact used by Boeyns and co-workers.[93,94]

Boeyns et al.[93] investigated the complexes $M_2(XYCCH_3)_4$ and $M_2(XYCCH_3)_4L_2$ [M = Rh, Pd, Cd, Cu; X, Y = S, O; L = H_2O, CH_3CSOH, $(CH_3)_2SO$, PPh_3]. A force field, calibrated on the basis of vibrational spectra[95] and including parameters for the above metals, was proposed. Calculations and experimental data led the authors[93] to the conclusion that the metal–metal distance in the above complexes is determined by steric factors both in the presence of the bond (Rh complex) and in its absence (Pd, Cu, and Cd complexes). A change in the nature of the steric influence can lead not only to a lengthening but also to a shortening of the metal–metal bonds.

However, in our view, such categorical conclusions concerning the predominant influence of the steric factor on the lengths of metal–metal bonds are not sufficiently justified. In the study of clusters, it is quite impermissible to neglect, as was done by Boeyns et al.,[93] the electronic factor and in the first place the orbital interactions of the metal atoms.

A similar approach was used in another study by Boeyns[94] to investigate high-order bonds in the complexes $Cr_2(CH_3)_8^{4-}$, $Mo_2(CH_3)_8^{4-}$, $W_2(CH_3)_8^{4-}$, and $Re_2(CH_3)_8^{2-}$. The force constants of the fourth-order metal–metal bonds as well as the parameters of the non-bonding van der Waals interactions were also calculated for the above atoms from experimental data.[96,97] The dependence of the energy of the steric strain of the complexes on the torsional angle of the metal–metal bond was examined. The stabilisation of the unfavourable eclipsed conformation is explained in this instance by the contribution of the δ-bonding component to the Cr–Cr bond (46 kJ mol^{-1}).[94] The properties of triple and quadruple W–W bonds were compared in relation to the complexes $W_2(O_2CC_2H_5)_4$ and $W_2(O_2CC_2H_5)_4(CH_2C_6H_5)_2$ and it was shown that, although the structures of these complexes are similar, the triple bond is significantly more mobile than the quadruple bond. The rotation about the Re–Re triple bond has been investigated[94] for the complex $Re_2Cl_4[P(C_2H_5)_3]_4$. It is claimed that in this case (in the absence of δ-bonding) the occurrence of the eclipsed conformation is caused by steric factors.

However, one cannot agree with all the conclusions reached by Boeyns,[94] because here too the role of orbital interactions has been clearly underestimated. In particular, one can hardly regard as correct the attempt to estimate (especially quantitatively) the effect of the δ-bond with the aid of the MMM.

VI. Simplified "mechanical" and geometrical models

Together with the MMM, simpler approaches based on "mechanical" ideas and geometrical models may be useful in the study of the steric structures of complexes. One of such approaches is the familiar Tolman method of conical angles θ (see, for example, Refs. 98 and 99) (Fig. 2). The method continues to be improved and has found extensive applications in quantitative estimations of steric factors in metal complexes.

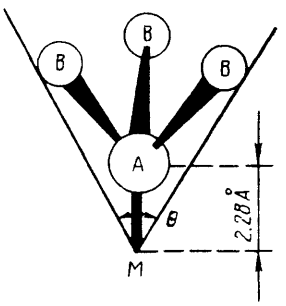


Figure 2. Tolman's conical angle model.

Thus a universal formula has been proposed[100] for the calculation of the conical angles of ligands of the type AB_n (A = atom coordinated to the metal; B = atom linked to A).

Similar formulae have been derived[101] for complex ligands of the type AB'_3, where B′ is a group of atoms. The effective covalent and van der Waals radii of the groups B′ and the conical angles of the ligands AB'_3 have been calculated from the available standardised data[99,102] for phosphorus-containing ligands PB'_3. The conical angles for 610 ligands of the type AB'_3 (A = N, P, As, Sb, Bi, C, Si, Ge, Sn, Pb; B′ = alkyl, cycloalkyl, aryl, alkylaryl, arylalkyl) have been published.[101,103] It was shown that the conical angles for Group IV and V elements are the same in the case of neighbouring elements A and decrease within the Group as the atomic number increases. It was noted that the conical angles depend little on the nature of the metal.

The attempt to extend to organic[104] and organoelement[105] compounds the above system for the description of the steric properties of substituents (ligands) in inorganic compounds is of interest. The attempt was based on the conical angles θ and derivatives of the "degrees of shielding" $\Lambda = \sin^2(\theta/4)$ with respect to these angles. The authors[104,105] derived simple formulae relating these parameters to the covalent radius of the central atom and published their values for various elements (H, B, C, Si, N, P, O, S, the halogens, and the transition metals). Thus a universal scale of steric constants for coordination, organic, and organoelement chemistry has been proposed.[104,105] Its undoubted advantages are

the uniqueness of the approach, a clear-cut geometrical significance of the parameters, and the ability in many instances to describe experimental data correctly.

However, one hardly agrees with the author's view that this system of constants is preferable to the familiar empirical scales of the E_s type, because both can be used only in those cases where the substituent is linked directly to the reaction centre (see, for example, Kuz'min and co-workers[14,15] and Gallo[106]).

Domrachev et al.[107] (see also Refs. 108 and 109) suggest that, not the conical angle, but the solid angle filled by the substituent R be used for the quantitative estimation of the degree of steric shielding of the metal atom in compounds of the type MR_n [R = PPh_3, CPh_3, η^1-Cp, η^5-Cp, CH_3, C_2H_5, CF_3, $C(CH_3)_3$, etc.]. Here the ligand atoms are specified as hard spheres with van der Waals radii. The sum of the solid angles of all the substituents (ligands) is used to estimate the steric strain in the complex. When it is exceeded (4π is the total solid angle), strain in the structure is indicated. The parameter described is satisfactorily correlated with data for the thermal stabilities of the compounds indicated.

In order to achieve a more correct estimation of the "non-valence interactions", it has been suggested[110] that these interactions be considered at the distance from the complex-forming atom where interligand contacts occur. The area S shielded by the ligand on the surface of a sphere with a radius r equal to the length of the metal–ligand bond is used as a steric characteristic of the ligand. The overall ligand environment of the metal is estimated by means of the expression $\sum_i S_i/4\pi r_i^2 \leqslant 1$. The closeness of this parameter to unity indicates, according to the author,[110] the existence of strain in the molecule (see also Refs. 107–109). The values of S calculated for a series of ligands have been published.[110]

Using, within the framework of the approach described, the parameters S, the same author analysed the structures of the metallocenes MCp_n (M = Be, Fe, Cr, V, Ti, Sc, Nd, Sm, Th, Zr, Hf, U; n = 2, 4) and discovered the factors determining whether the η^1- or the η^5-coordination of the cyclopentadienyl group is preferred.[111] This approach has been used[112] to estimate the relative stabilities of various isomers of the complex $Ca(BH_4)_2.2.(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$.

The sum of the solid angles of the ligands (SAS), normalised with respect to 4π, has been used for the quantitative estimation of the steric factors governing the stabilities of uranium complexes with the general formula $U(Cp)X_3L_n$ {X = CNS; n = 1, L = $CH_3OCH_2.CH_2OCH_3$; n = 2, L = $CH_3CON(CH_3)_2$, tetrahydrofuran, $P[N(CH_3)_2]_3O$; X = Cl, Br; n = 1, L = $Ph_2(O)PCH_2P(O)Ph_2$; n = 2, L = $(CH_3)_2CCON(CH_3)_2$, $POPh_3$}.[113] The authors isolated the region of the optimum shielding (SAS = 0.81) of the metal atom (the optimum packing of the ligands in the coordination sphere). With decrease or increase in the degree of shielding, the complexes become unstable.

In the study of lanthanide complexes $LnCp_3(NCR)_2$ (Ln = La, Ce, Pr; R = CH_3, C_2H_5), an additional term taking into account the radius of the metal atom is introduced into the SAS parameter.[114] It was shown that the size of the central atom influences significantly the stability of the complex and that lanthanum compounds are the most stable. The most favourable configuration of the ligand environment, corresponding to the optimum value SAS = 0.72, was discovered.

An attempt has been made[115,116] to use similar ideas not only for the quantitative estimation of the steric effect but also for the prediction of the geometries of the complexes. A model based on the principle of closest packing of the ligands (represented by solid cones with the apex at the centre of the metal atom) in the coordination sphere has been proposed. In terms of mathematical procedures, this approach is a vector analogue of the SAS model (for further details, see Xing-Fu, et al.[115]). Using the conical model, the structures of more than 50 compounds of the type MA_4, MA_3B, MA_2B_2, MAB_2C, and MABCD were calculated (M = actinides, lanthanides, and Group IVB metals). The results agree well with X-ray diffraction data. It has been shown[116] for the formation and dissociation reactions of complexes (see above) that the conical model is applicable to the study of the influence of steric factors on the possible direction of the process. More than 160 lanthanide complexes have been studied with the aid of the conical model.[117]

However, the postulates of the conical model have been developed most fully in the concept of the "coordination site" described in a series of investigations.[118–122] According to this model, not only ligands but also the conical "sites" which they can occupy may be described with the aid of the solid (or conical) angle. A "diagram of levels" is constructed on the basis of the determination in the coordination sphere of the metal atom of "first-order, second-order, etc. 'coordination sites'" (by distributing the Tolman cones in the "holes" within the close packing of the coordination sites of the previous order). The degeneracy of the "levels" in the presence of molecular symmetry and their alteration following the deformation of typical coordination polyhedra have been considered.[118]

The concept of "pre-bonding molecular structure", calculated from the level diagram in terms of the approximation of spherical (the halogens) and disc (Cp) ligands, has been introduced.[19] In order to estimate the correspondence between the ligand and the coordination site, the seat function is introduced:

$$F = \sum_i^m K_i (S_i - \theta_i)^2, \quad F' = \sum_i^m K_i (S_i - \theta_i)^2/\theta_i^2,$$

where m is the number of ligands, K_i the rigidity coefficient, S_i the conical angle of the "site", and θ_i the conical angle of the ligand (K = 1, $S \geqslant \theta$, K = 5, $S < \theta$).

With the aid of the proposed model, it has been possible[118–122] to explain the occurrence of disproportionation reactions, the distribution of ligands between the anion and cation in complex salts, thermolysis, racemisation, and a series of other reactions characteristic of actinide complexes.

However, we may note that all the models described above are suitable only for mononuclear coordination compounds. An approach, similar to that of Lobkovskii[110] and Bagnall and Xing-Fu,[113] based on the construction of projections of the ligands onto a cylindrical surface with a unit radius whose axis coincides with the M–M bond, has been proposed[109] for dinuclear complexes.

A general approach, suitable for polynuclear complexes containing a metal chain or a metallocycle has been put forward.[123] A closed continuous surface covering the metal atoms is constructed in accordance with specific rules. Next, the total area S of this surface is determined as well as its component S_e shielded by the ligands. A characteristic of the degree of shielding of the metallic core is the ratio $K = S/S_e$. Polynuclear complexes of Ti, V, Hg, Ge, Pt, Fe, Mn, and Cr were investigated within the framework of this model. It was shown that, by selecting appropriate ligands, it is possible to achieve the stabilisation of the required structure of the core. It has been suggested that the approach described can be used to study clusters with two-dimensional and three-dimensional structures.

The "frontal steric effect" model has been used successfully[124] to estimate the steric factors governing the stability of complexes. According to this model,[125] the steric effect of the substituent is proportional to the area which it occupies on a spherical surface separating it from the reaction centre. A computational scale of steric constants has been introduced: $R_S = 30 \lg \left(1-\sum_i r_i^2/4L_i^2\right)$, where r_i is the atomic radius of the ith atom in a complex substituent and L_i is the distance from the ith atom to the reaction centre.

This model has been used to investigate the complexes $(R_2PSS)_2M$ (M = Ni, Cu; R = various cyclic and acyclic substituents).[124] Comparison of the calculated results with the stability constants of the complexes[126] showed that, within the framework of individual reaction series, their stability is controlled by the steric factors of the substituents (a satisfactory correlation with the parameter R_S is observed).

An attempt has been made[127] to create on the basis of molecular-mechanical ideas a so called general model of the coordinate bond. According to this model, the length of the metal–donor centre bond is determined by the energy balance of the coordinate bond proper (described by the Morse potential) and the van der Waals interactions in the ligand environment. On the basis of this approach, the authors were able to explain the observed differences between the "long" and "short" Ln–H_2O bonds in the complexes $Ln(C_2H_5SO_4)_3.9H_2O$ and also the variation of the length of these bonds in the La–Lu series.

Table 1. The force fields used in calculations for metal complexes.

Metal	Ligand atoms	Allowance for the contributions of different interactions to the conformational energy				Refs.
		val	angle	tors	nb	
Co	H, C, N, O, S, B, P, Cl	+	+	+	+	[6]
	H, C, N	+	+	−	−	[37]
Cu	H, C, N, O, S, B, P, Cl, F	+	+	+	+	[6]
	H, C, O	+	−	−	+	[93]
Ni	H, C, N, O, S, B, P, Cl, F	+	+	−	+	[6]
Cd	H, C, O, S, P	+	+	+	+	[93]
Rh	H, C, O, S, P	+	+	+	−	[93]
Pd	H, C, O, S, P	+	+	+	+	[93]
Cr	C	+	−	−	−	[94]
Mo	C	+	−	−	−	[94]
W	C	+	−	−	−	[94]
Re	H, C, P, Cl	+	−	−	−	[94]
Eu	H, C, N, O	+	+	+	+	[61]
Yb	H, C, N, O	+	+	+	+	[61]

Notation adopted: val—bond deformations: angle—bond angle deformations; tors—torsional strain; nb—non-bonding interactions; + parameters are present; −parameters are absent.

A novel mechanical model has been used[128] to investigate the elementary steps in the synthesis-decomposition reactions of diarenechromium compounds. The $Cr(\eta^6\text{-}C_6R_6)_2$ (R = H, CH_3) molecules were represented by three-particle systems in which the benzene rings were represented by toroids of rotation. The metal–ligand interactions were described by the Morse potentials and the non-valence interactions by functions of the Lennard-Jones type. In all probability, this approach can be applied in a qualitative analysis of the stabilities and structures of the given systems.

As can be seen from the examples examined, the simplified mechanical models of complexes can be employed only in those cases where the steric strain of the molecules is determined primarily by the non-valence interactions between the ligands. In all probability, such approaches cannot be used correctly if the behaviour of the complexes is influenced significantly also by the structures and conformational characteristics of the ligands which are modelled, as a rule, by hard cones or spheres in such approaches. The mechanical models described can be used only when the principle of uniform filling of the coordination sphere by the ligands holds.

Thus analysis of the literature on the application of the MMM to the study of steric factors regulating the structures and properties of transition metal complexes shows that calculations of this kind make it possible to obtain much useful information. The method of molecular mechanics is at present available for the study of a wide range of compounds with various metals (Table 1 presents data for the known force fields). It is important to emphasise that, when the method is used correctly, a satisfactory agreement is achieved with the experimental results and in many instances it becomes possible to predict the properties of complexes.

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The use of Langmuir–Blodgett films as recording layers in optical information carriers

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ABSTRACT. The review deals with methods of recording and reproducing information for external computer memory devices in which Langmuir–Blodgett films are used as carriers and also with the physical effects occurring in these films, which may be used in the future for the creation of new superdense optical information carriers. Attention has concentrated on the photochromic reactions in the *J*-aggregates of Langmuir–Blodgett films, which permit the reversible recording of information. In many cases the preparation of the carrier and the technical characteristics of the corresponding memory devices are described in detail. The review considers the original studies and patents on this topic which have been published during the last 15 years.

The bibliography includes 55 references.

Contents

I.	Introduction	1106
II.	Archive recording	1107
III.	Reversible recording	1109
IV.	Recording of information by an electron beam on a Langmuir–Blodgett film with mobile ions	1114

I. Introduction

The problem of creating information carriers for optical reversible memory devices (MD) on computers as well as improvement of the density of the recording in such devices are of extremely great current interest. The optical memory devices of the archive type widely used nowadays do not provide for the local deletion and re-recording of information. The first reversible optical memory devices which became commercially available are memory devices with thermomagnetic recording and magnetooptical reproduction based on the Kerr and Faraday effects[1].

Numerous procedures for the recording and reproduction of information based on new principles as well as information carriers with recording layers having a wide variety of compositions, in particular with film recording layers prepared by the Langmuir–Blodgett method[2], have been proposed recently.

The Langmuir–Blodgett films (LB films) consist of layers of amphiphilic molecules (i.e. molecules having hydrophilic and hydrophobic components), which are ordered at the molecular level. They are transferred successively from the surface of a liquid subphase onto a solid support.[3]

The apparatus for the preparation of LB films is illustrated in Fig. 1. The process involving the deposition of a LB film begins with the deposition onto the surface of a liquid which is a solution of an amphiphilic substance in a volatile inert solvent at a concentration of the order of 0.1%. After the solvent has been evaporated, a monomolecular film consisting of molecules oriented uniformly with respect to their hydrophilic and hydrophobic groups in relation to the surface of the liquid is produced. The film is then removed by a mobile barrier, whilst monitoring the surface tension.

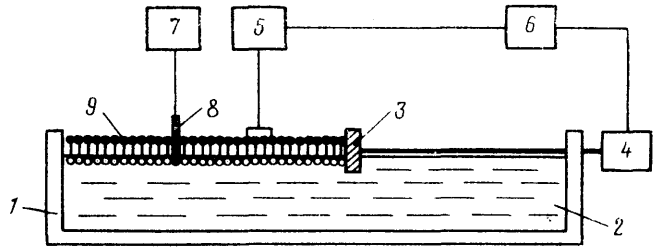


Figure 1. Schematic illustration of the apparatus for the deposition of Langmuir–Blodgett films on a solid support: *1*, bath; *2*, doubly distilled water; *3*, mobile barrier; *4*, motor driving the barrier for the compression of the monomolecular film; *5*, balance for the measurement of surface pressure; *6*, feedback device for monitoring the surface pressure; *7*, system for the lowering of the support; *8*, support; *9*, LB film.

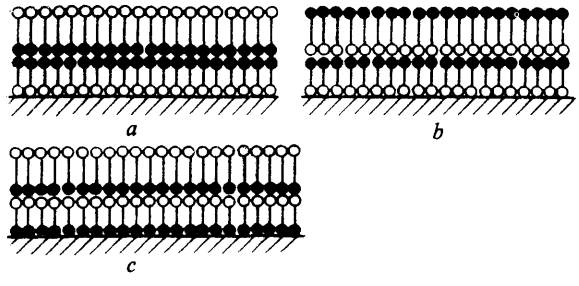


Figure 2. The structures of the Y-type (*a*), X-type (*b*), and Z-type (*c*) LB films

After the attainment of a certain film surface area, a sharp break appears on the plot of the surface pressure against the area per molecule, indicating the formation of a close-packed monolayer.

At the break point or at a somewhat lower surface pressure, the support is passed through the film and the amphiphilic molecules are deposited on the support with retention of their packing and orientation. If the support is hydrophobic, then the first layer of molecules is oriented with the hydrophobic ends towards the support and if it is hydrophilic the reverse orientation occurs. By repeating successively the procedure described, it is possible to deposit up to several hundred monolayers on the support. Depending on the deposition conditions, it is possible to obtain centrosymmetrical LB films of the Y type (Fig. 2*a*) with the opposite orientation of the molecules in neighbouring layers, or non-centrosymmetrical LB films of the X type (the hydrophobic ends of the molecules adjoin the support) (Fig. 2*b*), or such layers of the Z type (the hydrophilic ends adjoin the support) (Fig. 2*c*).

The constantly growing interest in the applications of LB films in a wide variety of engineering fields such as molecular electronics[4–7], optoelectronics[8–11], gas sensors[12–14], as lubricants for magnetic memory devices[15], in molecular engineering[16–18], etc. can be explained by a whole series of their unique properties such as an accurately specified thickness, which can be controlled to within a few angstroms, a high degree of homogeneity, and a constant mutual orientation of the molecules and their functional groups. It is then possible to create assemblies of molecular layers and individual molecules of any architecture.

The possibility of controlling the orientation of the molecules and the interaction between them at rigorously controlled distances makes it possible to achieve a reversible optical memory in LB films. The recording processes in such films can be of two types — chemical and orientational. The former are divided into intramolecular transformations (for example *cis–trans* isomerisation[19]) and chemical reactions of neighbouring molecules in one monolayer (for example, dimerisation[20] and polymerisation[21]) and in neighbouring monolayers, while the latter can be divided into *J*-aggregation processes[22,23] (i.e. rearrangements of an elementary two-dimensional cell of the LB film), degradations of *J*-aggregates[24,25], the reversible phase transitions of various kinds, including those involving the appearance of photodichroism under the influence of polarised light[26].

The recording processes based on chemical reactions make it possible to achieve a satisfactory permanence of the information and a high signal/noise ratio in the corresponding memory devices, but here it is difficult to achieve a reversible recording. Recording layers based on spiropyrans, in which a reversible structural rearrangement under the influence of UV and visible radiation can be readily achieved, are an exception[27].

The greatest stability of the recording layer can be attained if it is subjected to preliminary polymerisation by irradiation with UV light or low-energy electrons, which can be done also without the degradation of the LB film[28–31]. Information can be recorded in such layers also by means of the degradation of the polymer.

In recent years attempts have been made to create multilayer polyimide LB films which are thermally stable up to 700 K. These will be the most thermally stable thin organic films among those known to date.

With the aid of photochemical recording, it is possible to ensure also the replication of recorded information. Thus the photodimers formed in LB films under the influence of optical radiation have both optical and physicochemical properties different from those of the individual molecules. When the mixed layer is deposited by the Langmuir–Blodgett method onto a monolayer which has already been modified, the dimers are arranged on dimers and individual molecules are arranged on individual molecules. Thus the subsequent layer replicates the information recorded on the preceding layer. The upper layer can be separated from the lower layer by placing on its surface a film of poly(vinyl alcohol) and then splitting off both films[32,33]

The recording processes based on changes in the orientation and the relative positions of the molecules in the LB film make it possible to achieve the reversible recording of information, but the corresponding memory devices cannot at present compete with magnetooptical memory devices as regards the permanence of the recording, the signal/noise ratio, and a number of recording/re-recording cycles. Furthermore, when LB films consisting of two and more coaggregates are used (which is frequently necessary in recording procedures based on *J*-aggregation and *cis–trans* isomerisation processes), the problem of the formation of domains in the LB film owing to phase separation in the mixed monolayer arises[34]. The molecules in such island domains behave in many respects like a single assembly, as a result of which the recorded bit is blurred and the signal/noise ratio in the corresponding memory devices is therefore reduced. In an attempt to overcome these phenomena, use is made of special conditions in the deposition of films from a non-densely compressed monolayer whereupon the LB film consists of a "two-dimensional liquid" or various stabilising additives incorporated in the monolayer which diminish the size of the structured domains by becoming distributed along their boundaries.

Briefly, a vigorous search for reversible optical systems based on the LB technology and for ways of modifying thermoptically is being prosecuted at the present time, which will undoubtedly yield positive results in the future. The principal advantage of an optical memory with a carrier based on LB films over a magnetooptical memory will apparently become the achievement of multicolour recording on photochromic LB films containing either dyes of several types with absorption bands in different spectral ranges, located in successive layers, or one dye in one layer with various photochromic groups attached to one molecule, or coaggregate dyes. Multicolour optical recording makes it possible to create memory devices with a recording density several times greater than in the usual optical memory devices by recording several bits of information simultaneously at a single location of the laser spot.

The review deals with the principal methods of recording and reproducing information on carriers prepared by the Langmuir–Blodgett method proposed recently, the specific compositions and methods of depositing recording layers, as well as the physicochemical processes occurring in LB layers. There is a prospect that these processes may be used to record information. The main bulk of the review is devoted to reversible systems, while among systems of the archive type only some are mentioned.

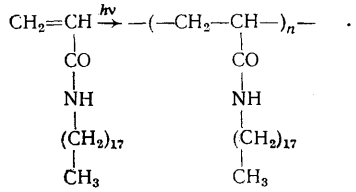
II. Archive recording

Archive memory devices do not allow the deletion and re-recording of information; they are designed for the long term storage of large amounts of information and belong to the so called "write once/read many" type in contrast to the reversible "write many/read many" memory devices. The principal requirements which must be met by archive devices is the greatest possible density of recording and the shortest possible access time to the data.

We shall consider certain physical principles on which information recording processes in these devices are based.

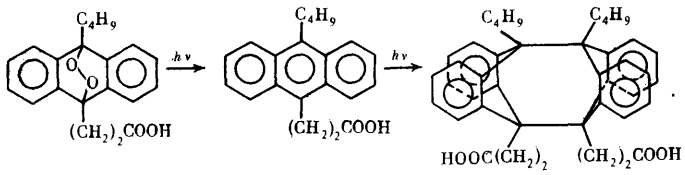
1. Photopolymerisation

Several systems have been proposed in which the local polymerisation under the influence of light is used to record information. An example of such a system has been examined in a study[21] where a stable polymer was formed under the influence of UV radiation in a LB film based on *N*-octadecylacrylamide as a result of the reaction



2. Photodimerisation

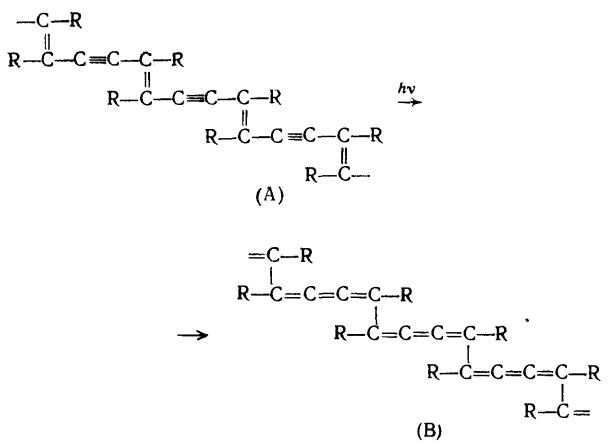
Intermolecular photodimerisation of neighbouring 9-anthryl-10-butyl-3-propanoic acid molecules has been used[20] to record information on a LB film:



This reaction proceeds in an arachidonic acid matrix with acid : matrix = 1 : 1 and 1 : 3 ratios under the influence of laser light with a wavelength of 420 ± 2.5 nm. The optical absorption spectrum of the film changes significantly under these conditions. The reverse reaction is not observed either in the dark or on irradiation with the light corresponding to the absorption band of the dimer over a period of 14 h.

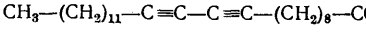
3. Photoinduced transformation of the polymer

An optical information carrier has been described[35] in which the acetylenic form (A) of polydiacetylene is converted into the butadiene form (B) under the influence of UV radiation:



The rate of recording on such films is 10^8 bits s^{-1} and the required energy density for recording is less than 800 J m^{-2}.

The carrier is prepared as follows. The monomer, for example pentacosa-10,12-diynoic acid



is deposited on the surface of water, buffered with $CdCl_2$ (10^{-4} M, pH 6.1), at 15 ± 0.1 °C by the Langmuir–Blodgett method. Chloroform, in which the acid concentration is 0.7 kg m^{-3}, is used as the solvent. 40 Monolayers of a Y-type LB film are deposited on a sulphuric acid-treated quartz glass support at a surface pressure of 25×10^{-3} N m^{-1}. This results in the formation of a coating having a thickness of the order of 1000 Å. Under the influence of 5 W m^{-2} UV radiation (λ = 240–400 nm), the acid polymerises in 40 min. The spectrum of the polymer then corresponds to the (A) form [Fig. 3, curve (*A*)]. On further irradiation with UV light up to a total dose of 100 J m^{-2}, the absorption spectrum changes [Fig. 3, curve (*B*)], indicates the conversion of the polymer into the (B) form. The recording of information is thus achieved. The change in the relative amounts of the polymers in the (A) and (B) forms as a function of the absorbed energy is illustrated in Fig. 4. The shorter the irradiation wavelength, the higher the efficiency of the (A)→(B) transformation.

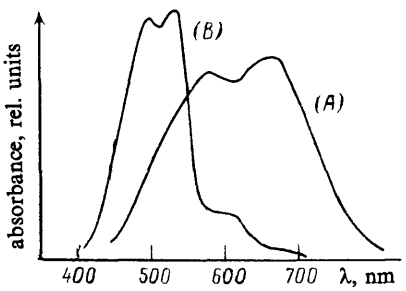


Figure 3. Absorption spectrum of a polydiacetylene LB film in the acetylene (A) and butadiene (B) forms.

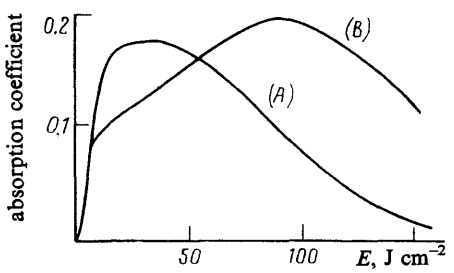


Figure 4. Variation of the relative amount of polyacetylene in the acetylene (A) (λ = 638 nm) and butadiene (B) (λ = 535 nm) forms as a function of the absorbed energy.

Archive devices with a carrier based on a LB film cannot as yet compete with the traditional optical discs, on which information is recorded by the photolithographic method, despite the simple

recording technology and the higher information density. The principal disadvantages of the recording procedures described above are the long photopolymerisation reaction and phototransformation times as well as the inadequate lifetime of the recorded information. Nevertheless studies are being conducted in order to reduce the photochemical reaction time in such systems[36] and also in order to stabilise the reaction products with the aid of different kinds of coaggregates.

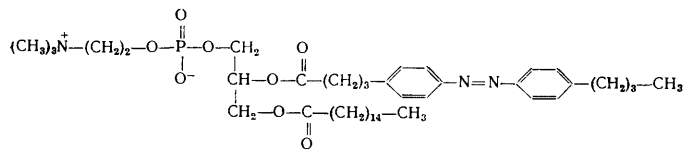
III. Reversible recording

The reversible methods for the recording of information are designed for external computer memory devices in which it is necessary to be able to delete the previously recorded information and to record new information. The principal requirements which must be met by such devices is the attainment of the largest possible number of recording–re-recording cycles as well as the greatest possible permanence of the recorded data. Reversible memory devices are divided into locally reversible, in which it is possible to re-record selectively over part of the existing information on the carrier, and others in which information can be re-recorded only after deleting the previously recorded information from the entire carrier. As regards the locally reversible memory devices, the latter are used widely at the present time with the information carrier in the form of magnetic discs with a realistically attainable recording density of 10^{10} bits m^{-2} as well as magnetooptical devices already prepared for mass production[1] with a recording density reaching 10^{12} bits m^{-2}.

1. Reversible recording without local re-recording

(a) *Cis–trans* isomerisation

LB films of photochromic phopholipids containing azobenzene have been investigated[19], for example:



When they are irradiated with UV light, *cis–trans* isomerisation (of azobenzene) takes place, the *cis*-isomer predominating in the film; on irradiation with visible light (at the wavelength λ = 540 nm), the *trans*-isomer predominates. The refractive index of the film then changes. By recording the modulation of the refractive index, it is possible to reproduce the recorded information. However, thermal equalisation of the relative amounts of the *cis*- and *trans*-isomers as a result of the reverse reaction is observed in this system, so that the proposed carrier is as yet difficult to use in memory devices.

It has been suggested that photochromic reactions, i.e. reactions involving a reversible change in the structure of molecules or in their electronic state under the influence of light accompanied by a change in the colour of the substance, have been proposed for the optical recording of information. This also entails as a rule a change in the refractive index of the film. Photochromic materials comprise a broad class of compounds—spiropyrans, metal dithizonates and metal-phthalocyanines, polycyclic hydrocarbons, etc. Since photochromic materials do not form a stable LB film, they are introduced into a matrix consisting of the film-forming substance, which is usually an aliphatic acid containing between 10 and 25 atoms together with stabilising additives. Sometimes the resulting film is also polymerised.

A large class of optical carriers, prepared by the Langmuir–Blodgett method and capable of the undergoing *cis–trans* isomerisation under the influence of light, has been described[37]. It includes photochromic materials with a N=N bond (azobenzene derivatives) or a C=C bond (indigo and thioindigo derivatives into which a hydrocarbon group, such as alkyl, alkoxy-, alkylacyl, or alkylamino-groups containing at least 10 and preferably 14–25 carbon atoms, has been introduced). We shall now list some of these compounds; for example, we have 4-monostearylamino-azobenzene, *N,N'*-distearylindigo, 5-octadecyl-5'-t-butylthioindigo, and 5-octadecyl-1,8-naphthylthioindigo. Aliphatic acids and their derivatives (stearic and arachidonic acids, methyl stearate, stearyl alcohol), tripalmitin, phospholipids etc. can be used as the film forming components necessary for the formation of the LB film. The molar ratio of the film forming component to the photochromic substance is varied from 1:1 to 6:1, the 1:1 and 2:1 ratios being most preferred. The solvents employed are benzene, chloroform, n-hexane, cyclohexane, and ethyl ether. The concentrations of the photochromic and film-forming substances in these solvents vary from 0.1 to 10 g m^{-3} (concentrations in the range 0.1–1 g m^{-3} being most preferred). The aqueous subphase is buffered by barium, calcium, or lithium salts at concentrations in the range 10^{-3}–10^{-5} M (pH 4–9). Acrylic resin is deposited on the recording layer in order to improve the operating characteristics of the carrier.

Several patented carriers will be examined below as specific examples[37].

Example 1. One of two mixtures—10^{-3} M solution of 4-monostearylaminoazobenzene in toluene or 10^{-3} M solution of a mixture of monostearylaminoazobenzene and stearic acid (in molar proportions of 1:2) in benzene—is irradiated with light at a wavelength of 360 nm. The irradiated solution (2.5×10^{-7} m^3) is deposited on water (pH 7, T = 18 °C) and the resulting film is compressed at a rate of 10 mm min^{-1} to the surface pressure $P_0 = 20 \times 10^{-3}$ N m^{-1}. After that, 30 monolayers of the film (750 Å) are deposited in succession on the support by the LB method. Information is recorded by means of a laser beam at a wavelength of 440 nm, focussed to a diameter of 1 μm. Before recording, the medium absorbs at a wavelength of 440 nm, while after recording it is transparent in this region. Information is retained for a fairly long time (for 30 days in the case of the carrier prepared from 4-monostearylaminobenzene and stearic acid).

Example 2. One of two mixtures—10^{-3} M *N,N'*-distearylindigo (the method of preparation has been described in a patent) in benzene or 1.5×10^{-3} M solution of a mixture of *N,N'*-distearylindigo and tripalmitin (molar ratio 1:2) in benzene—is irrigated with light at λ = 580 nm. The irradiated solution (2×10^{-7} m^3) is deposited on water (pH 5.8; T - 18 °C) and the resulting film is compressed at a rate of 1.6×10^{-4} m s^{-1} to the surface pressure $P_0 = 25 \times 10^{-3}$ M m^{-1}. Next, 20 monolayers of the film are deposited by the LB method on a hydrophobic glass carrier (treated in cadmium arachidate) by the LB method. The recording is performed with a laser at a wavelength of 440 nm. Before recording, the medium is transparent in the region of 540 nm, but after irradiation it becomes absorbing. The absorption spectra of the carrier containing *N',N'*-distearylindigo and tripalmitin, before and after recording, are illustrated in Fig. 5.

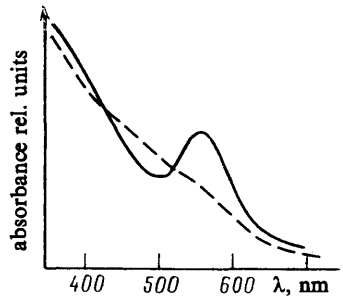
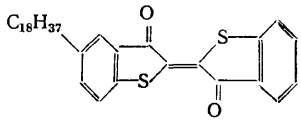


Figure 5. Absorption spectra of a carrier containing *N,N'*-distearylindigo and tripalmitin before recording (dashed line) and after recording (continuous line) with a laser operating at a wavelength of 440 nm.

Example 3. A solution of 5-octadecylthioindigo (10^{-3} M) (the method of preparation has been described in a patent[37]), i.e.



in benzene is irrigated with light at λ = 560 nm. The irradiated solution (3×10^{-7} m^3) is deposited on the surface of water (pH 5.2; T = 18 °C) and the resulting film is compressed at a rate of 1.6×10^{-4} m s^{-1} to the surface pressure $P_0 = 20 \times 10^{-3}$ N m^{-1}. Next, 20 monolayers are deposited on a hydrophobic glass support (treated with cadmium arachidate) by the LB method. The recording is carried out at a wavelength of 560 nm. The absorption spectra before and after irradiation are presented in Fig. 6.

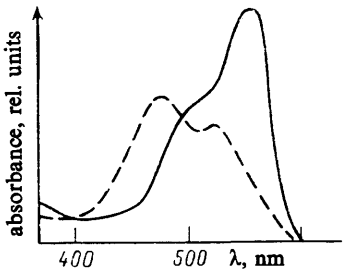
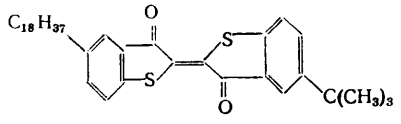


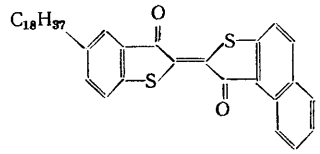
Figure 6. Absorption spectra of a carrier based on 5-octadecylthioindigo before recording (dashed line) and after recording (continuous line) at a wavelength of 560 nm.

Example 4. A solution of a mixture of 5'-t-butyl-5-octadecylthioindigo (0.5×10^{-3} M) i.e.



and tripalmitin (molar ratio 1:2) in chloroform is irradiated with light at a wavelength of 550 nm and 20 monolayers of the film are deposited on a chromium-plated support treated with cadmium arachidate. The recording is carried out a wavelength of 450 nm. The medium is transparent at a wavelength of 450 nm before recording and absorbs in this region after recording.

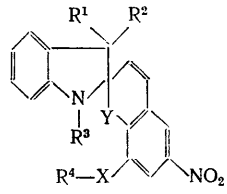
Example 5. A solution of 5-octadecyl-1,8-naphthalthioindigo (0.5×10^{-3} M), i.e.



and tripalmitin (molar ratio 1:2) is irradiated with light at a wavelength of 600 nm and 30 monolayers of the film deposited by the LB method on a glass support treated with cadmium arachidate. The recording is performed at a wavelength of 480 nm. Before irradiation, the medium absorbs in the region of 480 nm and after irradiation it is transparent in this region.

(b) Photochemical reactions in *J*-aggregates of organic dyes

The optical carriers described in patents[38–40] contain *J*-aggregates of spiropyrans of the type



where R^1 and R^2 are long alkyl group, R^3 is an alkyl group containing at least 10 and preferably 14–24 carbon atoms (hexadecyl, octadecyl, etc.), X is a single bond or one of the groups $-C_nH_{2n}OCO-$, $-C_nH_{2n}COO-$, $-C_nH_{2n}NHCO-$, $-C_nH_{2n}-CONH-$, or $-C_nH_{2n}O-$, where $n \geqslant 0$ (the $-CH_2OCO-$ or $-O-$ groups are most preferred), R^4 is an alkyl group containing at least one carbon atom, and Y=O or S. Among spiropyrans, the following are more preferred: 8-methoxy-3,3'-dimethyl-6-nitro-1'-octadecyl[2*H*-1-benzopyra-2,2'-indoline] and 8-dodecasonyloxy-3,3'-dimethyl-6-nitro-1'-octadecylspiro[2*H*-1-benzopyran-2,2'-indoline].

These spiropyrans, deposited on a carrier by the LB method, give rise to *J*-aggregates on heating[27,41–43]. The aggregates have narrower absorption bands than the unreacted dye, which makes it possible to increase the sensitivity of the method. The absorption bands undergo a bathochromic shift on formation of the *J*-aggregates.

The carrier can consist of dyes of two and more types[39]. Information is then recorded by means of laser beams at different wavelengths focussed in one spot.

On exposure to UV radiation, the spiropyrans photomerise to the corresponding photomerocyanines having maximum absorption peaks in the range 400–700 nm. However, these photomerocyanines are unstable and are usually reconverted into the initial spiropyrans even in the dark. On the other hand, if the

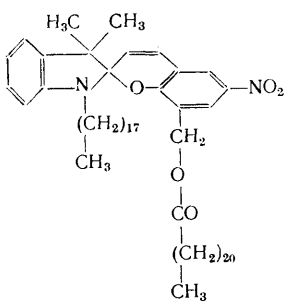
photomerocyanines are converted into *J*-aggregates as a result of a thermal reaction, the latter become more sensitive.

Aliphatic acids or their salts with polar groups are used to stabilise photomerocyanines in a LB film. One should use preferably acids with 14–24 carbon atoms (myristic, pentadecanoic, palmitic, heptadecanoic, stearic, nonadecanoic, behenic, etc.).

The solvents employed are chloroform, benzene, toluene tetrahydrofuran, acetonitrile, acetone, ethanol, etc. The solute concentrations are in the range 0.1–3 wt.%.

We shall now examine several specific examples.

Example 1. A solution of the spiropyran (3 M) (the method of preparation has been described in a patent[38])



and n-octadecane (in molar proportions of 1:2) is deposited on the surface of an aqueous subphase (pH 7.2; T = 18 °C). Next, 12 monolayers of a Y-type film are deposited on a hydrophobic glass [treated in a 10% (by volume) solution of chlorotrimethylsilane in toluene for 30 min] by the LB method. The absorption spectrum of the resulting film is illustrated in Fig. 7 (curve *A*). After the film has been irradiated with UV light for 10 min, a peak appears in the spectrum in the region of 583 nm, which is characteristic of photomerocyanine (curve *B*), while after heating by IR irradiation to 35–40 °C, *J*-aggregates appear (curve *C*). During the recording of information by means of a laser at a wavelength of 618 nm and an energy density of 5×10^3 J m^{-2}, there is a local reconversion of the photomerocyanine into the spiropyran (the absorption spectrum *A* is restored). Information is read by means of a laser beam with an energy density of 50 J m^{-2} and is deleted by UV light and heating. Information is not lost in the course of 5000 h and longer.

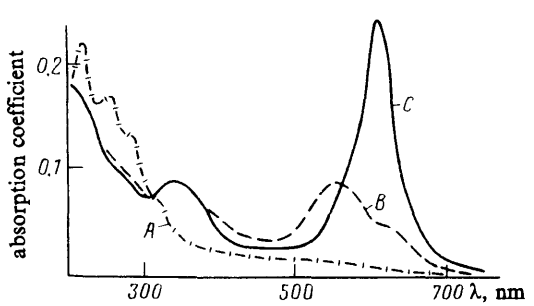
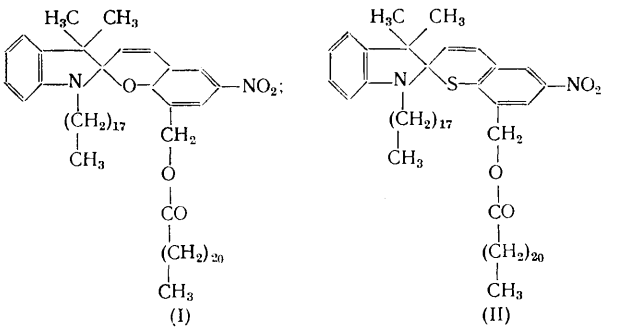


Figure 7. Absorption spectra of a LB film in a mixture of a spiropyran[39] and n-octadecane (molar ratio 1:2) before irradiation with UV light (*A*), after irradiation (*B*), and after additional heating by IR radiation to 35–40 °C (*C*). Heating results in the formation of *J*-aggregates of the corresponding photomerocyanine; (I) and (II)—dyes (see text).

It is also possible to record information by the conversion of the spiropyran into photomerocyanine[40].

Example 2. Two spiropyrans[39]



are deposited in succession on a carrier: 1 mmol of the spiropyran and 2 mmol of n-octadecane are dissolved in chloroform, 7×10^{-7} m^3 of the solution is deposited on the surface of an aqueous subphase buffered with sodium phosphate (pH 7.2; T = 18 °C), the resulting film is compressed to the pressure $P_0 = 20 \times 10^{-3}$ N m^{-1}, and 20 Y-type monolayers are deposited by the LB method on a hydrophobic glass support treated in 10% solution (by volume) of chlorotrimethylsilane in toluene for 30 min. The same procedure is gone through with the second spiropyran.

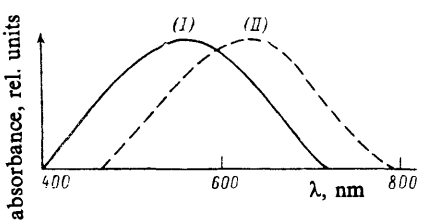


Figure 8. Absorption spectra of a carrier consisting of two spiropyrans[39] after their conversion into the corresponding photomerocyanines as a result of UV irradiation.

After this, the carrier is irradiated with the light from a UV lamp (at a wavelength of 350 nm) for 10 min. This results in the formation of photomerocyanines whose absorption spectra are illustrated in Fig. 8. (When two and more dyes are used, it is essential that their maxima should differ by at least the half-width of the absorption peak of the *J*-aggregates, i.e. by 20–30 nm.) The carrier is then heated by an IR lamp to 35–40 °C for 15 min. The spectra of the resulting *J*-aggregates are shown in Fig. 9. Evidently the peaks undergo a bathochromic shift by 35–50 nm and are narrowed to a half-width of about 30 nm.

The recording is carried out by means of two lasers operating at wavelengths of 618 and 653 nm and with an energy density of 5×10^3 J m^{-2}. Information is read by the same lasers at an intensity of 50 J m^{-2}.

Information is deleted by UV irradiation and by heating the carrier.

Yet another class of photochromic materials, whose complex molecule contains benzothiopyran, has been described[44]. A non-irradiated LB film with the photochromic substance has no absorption peaks in the range 500–900 nm, while the film irradiated with UV light absorbs strongly in the range 600–850 nm. The carrier consists of three layers—recording, refracting, and reflecting. A laser operating at a wavelength of 780 nm and with a power of 7.5 mW is used for recording. The sensitivity of the recording for a 20% change in the reflectance is 1.5×10^3 J m^{-2}. The signal/noise ratio in the reproduction of the information is 54 dB.

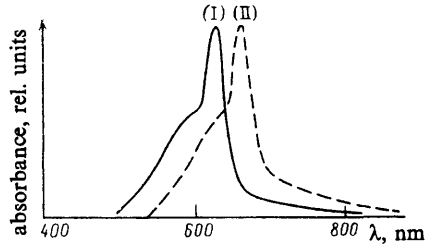
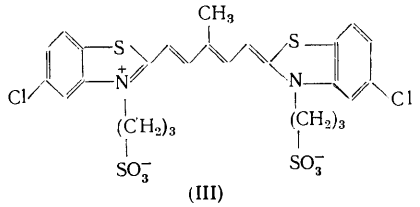
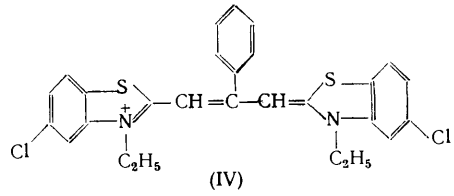


Figure 9. Spectra of photomerocyanines after the formation of *J*-aggregates; (I)–(II)—dyes (see text).

Multicolour carriers based on dyes containing *J*-aggregates have been proposed[24,45]. The following dyes are most preferred:





At least two of the following three substances are employed as the film-forming materials: dioctadecylammonium chloride (DODAC), stearylamine, and methyl stearate. It is possible to use arachidonic acid alone.

Example 1. The dye (III), stearylamine, and methyl stearate (molar ratios 1:1:3, overall concentration of stearylamine and methyl stearate 10^{-9} kg m^{-3}) in the 4:1 chloroform–methanol mixed solvent is deposited on the surface of water at 16 °C and the layer is compressed to surface pressure $P_0 = 35 \times 10^{-3}$ N m^{-1}. Next, 25 monolayers of the film (800 Å) are deposited by the LB method on a glass support coated by a layer of aluminium (2000 Å).

The recording is performed with a semiconductor laser operating at a wavelength of 780 nm, with a power of 6×10^{-3} W and with a pulse duration of 10^{-7} s. The *J*-aggregates undergo local decomposition under these conditions. The absorption spectra of such a mixture before and after recording are illustrated in Fig. 10.

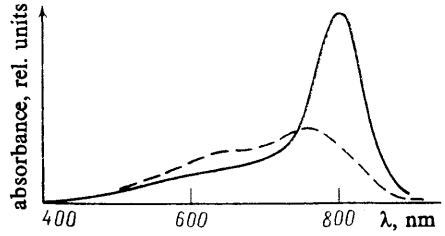


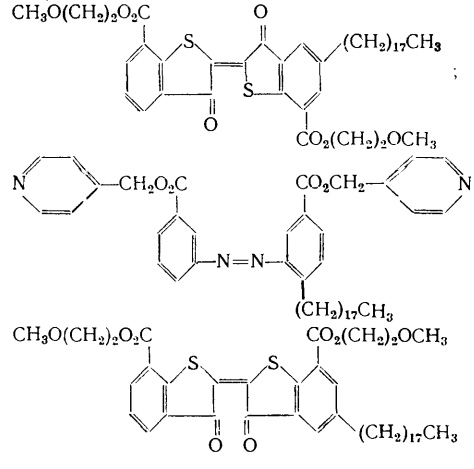
Figure 10. Absorption spectrum of the dye (III), stearylamine, and methyl stearate (molar ratio 1:1:3) in a LB film before recording (continuous line) and after recording (dashed line) with a laser operating at a wavelength of 780 nm. Irradiation results in the local decomposition of *J*-aggregates.

Example 2. A LB film of the dye (IV) and arachidonic acid (molar ratio 1:2) is deposited on top of the recording layer prepared as described in example 1. The film is compressed on the surface of water (T = 16 °C) to the surface pressure $P_0 = 30 \times 10^{-3}$ N m^{-1} and 6 monolayers of the film (200 Å) are deposited. The recording is performed with two lasers having a power of 3.5×10^{-3} W and operating at the wavelengths corresponding to the absorption peaks of the two dyes—at 670 and 780 nm.

(c) Photochemical liberation of the metal

The photochemical liberation of the metal in the LB film has been proposed in a number of studies[46–51] as reversible reaction.

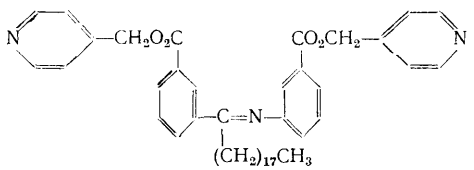
Example 1. One of the substances below[46–48], i.e.



is dissolved in $CHCl_3$ and deposited on an aqueous subphase buffered with $AgNO_3$ (pH 5.2). After the evaporation of $CHCl_3$, between 1 and 25 monolayers of the film are deposited by the LB

method on a glass support, the film being simultaneously irradiated with light at a wavelength of 450 nm. The recording is carried out with a laser operating at a wavelength of 550 nm. The absorption peak at 620 nm changes under these conditions. The reading of information is also based on this peak. Information is deleted by laser light at a wavelength of 450 nm in the course of 3 min.

Example 2. The substance



is dissolved in $CHCl_3$ and is deposited on the surface of an aqueous subphase containing Cu^+ ions (pH 5.2). After the evaporation of $CHCl_3$, between 1 and 25 monolayers of the film are deposited by the LB method on a glass support, the film being simultaneously irradiated with light at λ = 313 nm. The recording is carried out by means of a laser beam at a wavelength of 450 nm and is read from the change in the peak in the region of 530 nm in the absorption spectrum of the film. Information is deleted by irradiation with light at λ = 313 nm for 3 min[49–51].

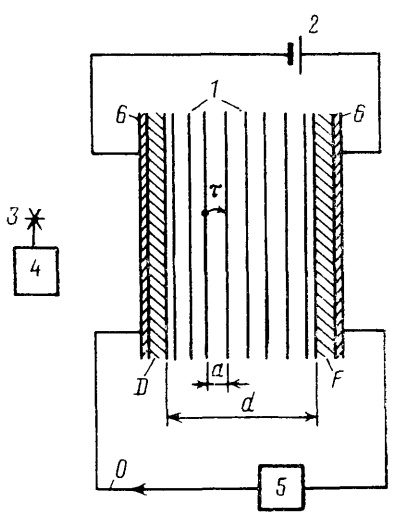


Figure 11. A multilayer carrier comprising polydiacetylene LB layers: *1*, carrier; *2*, source of supply; *3*, laser; *4*, modulator; *5*, optical amplifier; *6*, electrodes; *D*—photoinjection layer; *F*—fluorescent layer; *O*—optical loop.

In conclusion of this Section, we shall deal with a fundamentally new method of recording information on a multilayer carrier prepared by the LB technology, which can be employed in operating memory devices.

(d) Photoelectron recording on a multilayer carrier

A patent[52] describes how diacetylene LB films, polymerised to achieve stability by UV or electron irradiation, are placed between a photoinjection layer *D* and a fluorescent layer *F* (Fig. 11).

The recording is carried out with a laser fitted with a modulator. During recording, electrons are emitted from the layer *D* and are then caused by the electric field, generated in a source connected via electrodes to the carrier, to jump from layer to layer for as long as the field operates. The *F* and *D* layers can be connected by the optical loop O fitted with an optical or electrical amplifier. The loop is used to maintain the supply to the *D* layer and makes it possible to store the recorded information for a long time.

An 8-layer information carrier, possibly containing an even greater number of layers, has been described[52].

We shall consider the behaviour of an electron after its emission from the *D* layer. Suppose that τ is the time taken for the jump to the next polydiacetylene plane, whereupon

$$1/\tau = \nu \exp(-2ka),$$

where ν is the background frequency, a the distance between the layers, and $k^2 = 2mA/h^2$ (A is the electron affinity of the layer and m the mass of the electron).

If a potential $V > V(h) = n^2 k_B T/e$, where n is the number of layers, k_B the Boltzmann constant, T the absolute temperature, and e the charge of the electron, is applied to the carrier then the drift along the field exceeds the diffusion of the electron over the distance a. Under these conditions, the energy difference between the electrons in neighbouring layers is greater than $k_B T$ and the reverse jump against the field beomes unlikely. For a film made up of 8 layers at room temperature, $V(h) \simeq 0.2$ V. When $a = 10^{-9}$ m, $A = 1.6 \times 10^{-19}$ J, and $\nu = 10^{14}$ Hz, the time τ between the jumps is 8.8×10^{-6} s. Thus, when a potential of 0.2 V is applied to the carrier, the electron injected into the first layer emerges from the 8th layer after 70 μs.

The laser beam is modulated in such a way that the pulse has a width t and a period t/n. The set of light pulses corresponding, for example, to the 10011010 datum is transformed into the presence or absence of a charge in the corresponding layer after a time t. The closed optical loop *O* makes it possible to increase the storage time. It is also possible to use several layers carrying a charge q_m per bit. The criterion indicating that neighbouring bits will not diffuse into one another after N cycles as described by the expression

$$V/V(h) > N/M^2,$$

where M is the number of layers used to store one bit of information.

In reading the information, it is possible to employ the current differentiation method instead of detection with the aid of the fluorescent *F* layer. The maximum current change is $\Delta I = q_m/n\tau$.

Figs. 12 and 13 illustrate another carrier made up of polydiacetylene bilayers of two types, differing in the electron affinity by $\Delta A \simeq 10 k_B T$. For the electron jumps illustrated in the figures by arrows, we have

$1/\tau_{12}(s) = \nu \exp(-2ka) \exp(-\Delta A/k_B T)$ in a weak field $E < \Delta A/(e.a)$;

$1/\tau_{12}(l) = \nu \exp(-2ka)$ in a strong field $E \geqslant \Delta A/(e.a)$;

$$1/\tau_{11} = \nu \exp(-4ka),$$

where τ_{12} is the time taken for a jump from a type *1* layer to a neighbouring type *2* layer in weak (Fig. 12) and strong (Fig. 13) fields and τ_{11} is the time taken for a jump from a type *1* layer to the nearest type *1* layer.

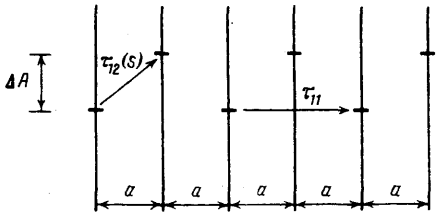


Figure 12. Schematic illustration of the energy levels of a carrier consisting of bilayers of polydiacetylene of two types differing in electron affinity ΔA by $\sim 10k_BT$ in a weak electric field ($E < \Delta A/ea$).

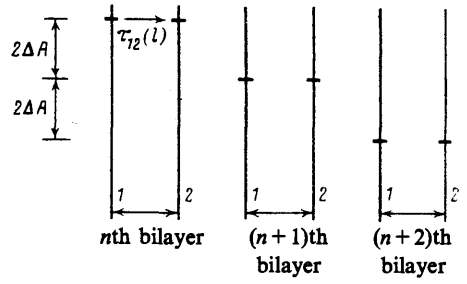


Figure 13. Schematic illustration of the energy levels of a carrier made up of polydiacetylene bilayers in a strong electric field ($E > \Delta A/ea$).

Thus $\tau_{12}(l) \ll \tau_{12}(s) \ll \tau_{11}$.

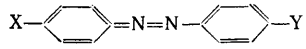
In the carrier described, one bit occupies one bilayer. For T = 300 K and $A = 10k_BT$, we have $\tau_{12}(l) = 8.8 \times 10^{-6}$ s, $\tau_{12}(s) = 0.19$ s, and $\tau_{11} = 2.17$ h.

The recording is carried out in a strong field $E = A/ea = 2.5 \times 10^8$ W m^{-1} for $A = 10k_BT$ at T = 300 K. It is stored in a weak or zero field for a time $\tau_{12}(s)$ and is read in a strong field. The storage time can be increased by using three layers for the recording of one bit (two layers of type *2* between insulated layers of type *1*). In this case, we obtain $\tau_{11} \simeq 20000$ years and $\tau_{12}(s) = 6000$ years at τ = 77 K.

2. Locally reversible recording

The creation of photochemical carriers with the possibility of local re-recording of information has been reported[53]. The carrier was made from 4-$RC_6H_4CH{=}CH{-}CH{=}CHCO_2H$ (V) (R = alkyl or alkoxy-group with 6–20 carbon atoms). For example, a quartz support coated by the LB method with 162 layers of the 2-*trans*, 4-*trans*-(V) mixture (R = n-octyloxy-group) produces a carrier with an absorption peak in the region of 300 nm. Irradiation with light at a wavelength of 300 nm diminishes the intensity of this peak and at the same time a new peak appears in the region of 270 nm. On the other hand, irradiation with light at a wavelength of 270 nm restores the peak in the region of 300 nm. Thus, using two lasers, it is possible to ensure the local re-recording of information.

As stated above, in reversible information carriers based on azobenzene derivatives[37] the reverse *trans*-isomerisation reaction is hindered because of the high energy of the re-packing of molecules in the monolayer. In order to overcome this difficulty and ensure the local re-recording of information, it has recently been suggested[54] that molecules of azobenzene derivatives, i.e.

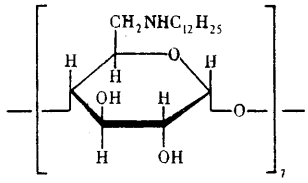


(a) X = H, Y = COOH;

(b) X = $(CH_3)_2N$, Y = COOH;

(c) X = $(CH_3)_2N$, Y = SO_3Na;

be incorporated within the cavity of the β-cyclodextrin molecule:



This seven-membered cyclic β-dextrin molecule is barrel-shaped and has an inner cavity approximately 50 nm in diameter. The *trans*-isomer of the azobenzene derivative and β-cyclodextrin (molar ratio 1:1) are deposited in the form of a LB film comprising 50 monolayers. The azobenzene molecule is then located within the β-cyclodextrin cavity in such a way that its long axis coincides with the axes of the aliphatic substituents in the β-cyclodextrin and the *cis–trans* isomerisation of azobenzene can be readily achieved on treatment with light in the visible or near UV regions.

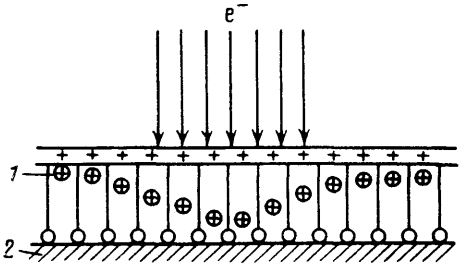


Figure 14. Carrier comprising a barium stearate LB film with mobile barium ions: *1*, barium ions; *2*, carbon base.

IV. Recording of information by an electron beam on a LB film with mobile ions

It has been proposed in a patent[55] that a LB film of barium stearate (Fig. 14) with mobile barium ions, deposited on a carbon base, be used as the information carrier. The LB film has an electrical surface potential of 100 mV relative to the base. If a

potential of +2.5 V is applied to the latter, then the excess barium ions migrate to the surface of the film.

Recording is achieved by means of an electron beam ($I = 10^{-10}$ A, $E = 1.6 \times 10^{-17}$ J, $d = 10^{-8}$ m). When it reaches the site where the information bit should be recorded (for example "1"), the potential of the support is reduced to zero by means of a synchronised potential source. A negative field gradient relative to the support is generated. However, it is insufficient for the migration of the ions to the support. Under the influence of the electron beam, the ions migrate into the bulk of the film. After the information bit has been recorded, the surface potential is reduced at this site by 0.1 V and the surface has a higher secondary emission coefficient. The information is read by secondary electron spectroscopic methods or by the diffraction of low-energy electrons using an electron beam with a current of $10^{-11}-10^{-12}$ A. The density of the recording reaches 10^{16} bits m^{-2}. Local deletion of information in this method has not so far been attained.

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Activation of C–C bonds in unsaturated hydrocarbons by metal complexes

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ABSTRACT. The current position of the problem of the activation of C–C bonds in alkanes and cycloalkanes is examined. The two main routes for the cleavage of unactivated single C–C bonds—metal-complex cleavage on an unsaturated coordinate metal site and electrophilic cleavage—are discussed. The literature data on the development of catalysts for the "low-temperature" cleavage of C–C bonds in alkanes are correlated.

The bibliography includes 158 references

Contents

I.	Introduction	1118
II.	Cleavage of C–C bonds in alkanes on a metal site	1119
III.	Novel superacid complexes—effective reagents and catalysts of low-temperature reactions of alkanes and cycloalkanes	1126

I. Introduction

A new stage in the chemistry of alkanes that could be called "the low-temperature chemistry of paraffins" began in the 1970s.

Activation of the C–H bonds of saturated hydrocarbons by transition metal complexes in solution[1] was discovered in 1969 and thus new possibilities for selective conversions of alkanes, including methane, under mild conditions were demonstrated. This area is undergoing rapid development at the present time.[2–15] In his introduction to the recently published issue of *New Journal of Chemistry* that is devoted to problems concerning the activation and functionalisation of alkanes, Hill writes that there are few problems in chemistry which would have stimulated greater interest during the last ten years than the selective conversions of alkanes. The reasons for this are clear. Alkanes constitute "the ultimate feedstocks for production of a myriad of organic products from pharmaceuticals and fibres to new and innovative materials".[15]

The second important milestone in the development of the low-temperature chemistry of alkanes is mainly connected with the discovery of new proton superacids whose acidity is greater than that of sulphuric acid by a factor of 10^7-10^{19}.[16–20] Because of the exceptionally high electrophilicity of the unsolvated proton in superacid media it was possible for the first time to carry out conversions of alkanes effectively at room temperature and lower temperatures.[16–26] Until recently proton superacids were the only reagents capable of cleaving not only the C–H bonds but also the more inert C–C bonds in alkanes under mild conditions.[27,28] By using superacid media it was possible to observe experimentally for the first time alkyl cations formed from alkanes,[16,21,22] which had previously been postulated as intermediates in organic reactions.

Another important contribution to the problem of the activation of alkanes has been made by the concept of the "pentacoordinate carbonium ion", which plays a key role in electrophilic attack on C–H and C–C σ-bonds.[19] Superacid activation of alkanes, to which a large number of publications have been devoted, will not be specifically examined in this review. We should only mention that the use of proton superacids is severely restricted by their limited availability, toxicity, and corrosive nature, and the difficulties in using them.

We also do not have the opportunity to dwell on the impressive progress achieved in a traditional area such as the gas-phase reactions of alkanes on heterogeneous metal and oxide catalysts, which as usual has played a leading role in industrial processes (see, for example, several studies).[29–40]

Table 1. Logarithms of equilibrium constants of the cracking reactions of alkanes and the dimerisation of olefins.*

Reaction	$\log K_p$, at T, K		
	300	500	700
$C_6H_{14} \rightleftarrows C_4H_{10}+C_2H_4$	−8.230	−2.230	+0.172
$C_7H_{16} \rightleftarrows C_5H_{12}+C_2H_4$	−7.846	−1.908	+0.608
$C_8H_{18} \rightleftarrows C_4H_{10}+C_4H_8$	−3.583	+0.367	+2.025
$C_8H_{18} \rightleftarrows C_5H_{12}+C_3H_6$	−5.442	−0.301	+1.853
$C_{10}H_{22} \rightleftarrows C_4H_{10}+C_6H_{12}$**	−5.758	−0.676	+1.468
$2C_4H_8 \rightleftarrows C_8H_{16}$**	+6.631	+0.915	−1.481
$2C_5H_{10} \rightleftarrows C_{10}H_{20}$**	+6.434	+0.736	−1.657

* Calculated from the results of Zhorov.[45]
** Alkene-1.

The aim of this review is to cover the recent progress in the low-temperature activation of the C–C bonds of alkanes by metal complexes.

It is well known that the carbon–carbon bond of paraffins is amongst the most passive of bonds of one of the most inert classes of organic compounds. Not long before the discovery of the metal-complex activation of the C–H bonds of alkanes, Halpern wrote that this problem presents a challenge to chemists.[41,42] This can apply even more to the activation of C–C bonds.

The ever increasing interest in a solution to this problem is governed by the key role of reactions involving cleavage of C–C bonds in industrial processes for the treatment of hydrocarbon raw materials (isomerisation, cracking, hydrocracking, etc.).

Cleavage of the thermodynamically stable non-polar C–C σ-bonds in paraffins, which do not have either free electron pairs or low-lying vacant orbitals, usually takes place effectively at high temperatures (300–1000 °C) in the gas phase.[43,44]

It follows from Table 1 that the cracking of alkanes at a low temperature is thermodynamically unfavourable. Only at elevated temperatures is the thermodynamic restriction lifted, but high-temperature processes consume considerable energy and are generally not very selective.

On the other hand the oligomerisation of olefins at low temperatures is accompanied by the liberation of sufficient heat to compensate the energy of cleaving the C–C bonds. Therefore the low-temperature cracking of alkanes is thermodynamically possible if it occurs with the formation of lower alkanes and oligomers.

At the present time it would appear that two routes for the activation of C–C bonds in alkanes resulting in their cleavage are of the greatest significance. The first is an electrophilic route which either involves the direct cleavage of C–C bonds by treatment with an electrophile E^+

$$R_3C{-}CR_3 + E^+ \rightarrow R_3CE + \overset{+}{C}R_3 \qquad (1a)$$

or the initial cleavage of C–H bonds to form carbocations or cation-like intermediates, which subsequently undergo intramolecular reactions with cleavage of C–C bonds:†

$$RH \xrightarrow[-EH]{E^+} R^+ \rightleftarrows (R')^+ + \quad \diagup C{=}C \diagdown \qquad (1b)$$

The second route for activating C–C bonds involves their interaction with unsaturated coordinate transition metal complexes, which can formally be represented as occurring via the insertion (oxidative addition) of complex M into the C–C bond:

$$\diagup C{-}C \diagdown + M \rightarrow \diagup C{-}M{-}C \diagdown \rightarrow \text{products.} \qquad (2a)$$

In this case as in the electrophilic cleavage of C–C bonds, 2 routes are actually possible. The first involves the direct insertion of the metal complex into the C–C bond [scheme (2a)], similar to that which occurs with the covalent bonds: H–H,[48–50] R–X,[48] Si–H,[51–53] and C–H.[2,5–7,9,10,54–62]

The second route involves the oxidative addition of C–H bonds to the metal complex followed by cleavage of the C–C bond in the resulting σ-alkylhydride complex:

$$R{-}CH_2{-}CH_3 + M \rightleftarrows RCH_2CH_2{-}M{-}H \qquad (2b)$$

α-elimination | β-elimination

$$\begin{array}{ll} H & CH_2{=}CH_2 \\ | & | \\ CH_2{=}M{-}CH_2R & R{-}M{-}H \\ \downarrow\uparrow & \uparrow\downarrow \\ CH_3{-}M{-}CH_2R & CH_3CH_2{-}M{-}R \end{array}$$

As will be demonstrated below, scheme (2b) is not just speculative.

† The formation of carbocations from hydrocarbons may possible occur in stages. Initially one electron is transferred to the electrophile to form E, then the transfer of $H^{\cdot}$ occurs.[46,47]

II. Cleavage of C–C bonds in alkanes on a metal site

During the last thirty years significant progress has been made in the use of transition metal complexes for activating inert covalent bonds,[48–64] and C–H bonds in paraffins. However, all of the known catalytic conversions of unactivated alkanes and cycloalkanes by transition metal complexes in the liquid phase relate only to C–H bonds and not C–C bonds. Cleavage of C–C bonds only occurs in strained cycloalkanes and in energy-rich polyhedranes (see the review of Crabtree).[6]

What is the reason for the high degree of inertness of C–C bonds compared to C–H bonds in alkanes? The energies of σ-bonds (in kcal mol^{-1}) are given below:[65,66]

H–H	C–H	C–C
104	96–105	87–90

It follows from this that the C–C bond is appreciably less stable than the C–H and H–H bonds. However, their reactivity increases in reverse order. Thus, molecular hydrogen is fairly readily activated by a large number of metal complexes while examples of the activation of C–H bonds in alkanes and cycloalkanes are quite well known although comparatively rare. On the other hand the catalytic cleavage of C–C bonds in paraffins by metal complexes in the liquid phase has until recently not been reported at all:

Increase in reactivity ←

H–H C–H C–C

→ Decrease in bond strength

The theory that the metal-complex cleavage of a C–C bond to form two weak C–M bonds, the energy of which does not compensate the energy of cleavage of the C–C bond, is thermodynamically unfavourable has been made widely known.[5,6] Thus, it follows from the experimental results of Halpern[5] that the energy of the Co–R bond in dimethylglyoximate complexes $RCo(dmg)_2$ and the R–Mn bond in the complexes $RMn(CO)_5$ and $RMn(CO)_4(PPh_3)$ is in the range 18–25 kcal mol^{-1}. Halpern assumes that for other metals of the 3*d* series (end of the period) the same order of magnitude of M–C bond energy is typical. At the same time the energies of the corresponding M–H bonds are 52–80 kcal mol^{-1}. It was concluded from this that the oxidative addition of the H–H bond to the metal site of a complex is exothermic while addition of C–H bonds is an endothermic process. The oxidative addition of C–C bonds to a metal complex is thought to be even more thermodynamically unfavourable. However, this does not appear to be a general conclusion. Judging by the small amount of data on the M–C bond energies in solution for certain transition metals of the 3*d* series (beginning of the period), 4*d* and 5*d* series, lanthanides, and actinides, these values are considerably higher than those quoted (see Tables 2 and 3). We should note that the energies of M–C bonds in cationic complexes is higher than in neutral complexes and is approximately equal to the energies of M–H bonds (Table 3). As will be demonstrated below, the energies of $M^+{-}CH_3$ bonds in the gas phase are higher than the energies of the corresponding $M^+{-}H$ bonds. Thus, the thermodynamic restrictions on the cleavage of C–C bonds with metal complexes are not obligatory. The thermodynamics of these reactions also depend to a large extent on the characteristics of the metal complex and in certain cases they can be exothermic.[74]

Table 2. Energies of M–Alk bonds.

Complex	M–C	Bond energy, kcal mol^{-1}	Refs.
RCoL(L')[a,b]	Co–CHR_2	28–25	[5]
Ado-B_{12}[c]	Co–CH_2R	32	[67]
$CH_3Mn(CO)_5$	Mn–CH_3	37	[68]
$(CH_3)_3PtCp$	Pt–CH_3	38	[69]
$CH_3IrClI(CO)(PMe_3)_2$	Ir–CH_3	46	[69]
$CH_3Re(CO)_5$	Re–CH_3	53	[70]
$(CH_3)_2TiCp_2$	Ti–CH_3	60	[71]
$(CH_3)_2ZrCp_2$	Zr–CH_3	66	[71]
$(C_4H_9)_2ThCp'_2$[d]	Th–C_4H_9	73	[72]
Alk(Alk')UCp'_2[d]	U–Alk	60–85	[72]

[a] L = pyridine, imidazole, PR_3; L' = dimethylglyoxime.
[b] L = pyridine; L' = *N,N'*-disalicylidene-*o*-phenylenediamine.
[c] Ado-B_{12} = adenosylcobalamine.
[d] Cp' = pentamethylcyclopentadienyl.

Table 3. Calculated energies of the M–C and M–H bonds in transition metal carbonyl complexes[73].

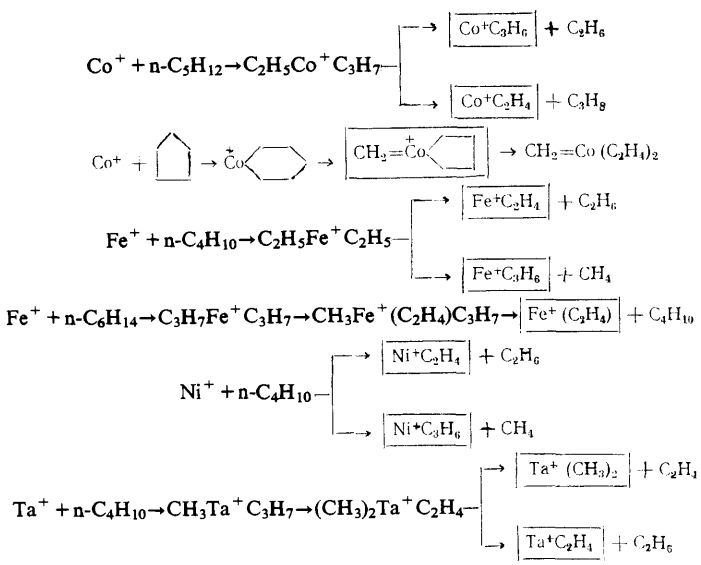
Complex	Energy of M–X bond, kcal mol^{-1}		Complex	Energy of M–X bond, kcal mol^{-1}	
	X=CH_3	X=H		X=CH_3	X=H
$XMn(CO)_5$	37	54	$XIr(CO)_4$	51	68
$XRe(CO)_5$	48	67	$XRe(CO)_5^+$	57	60
$XCo(CO)_4$	38	55	$XNi(CO)_4^+$	60	62
$XRh(CO)_4$	45	61			

These conclusions are supported by the literature data on the cleavage of C–C bonds in alkanes and cycloalkanes on a "ligand-free" metal site. These data will be examined below. On the other hand, all of the experimentally obtained material indicates the outstanding importance of steric factors in the attack by a metal complex or metal on a C–C bond.

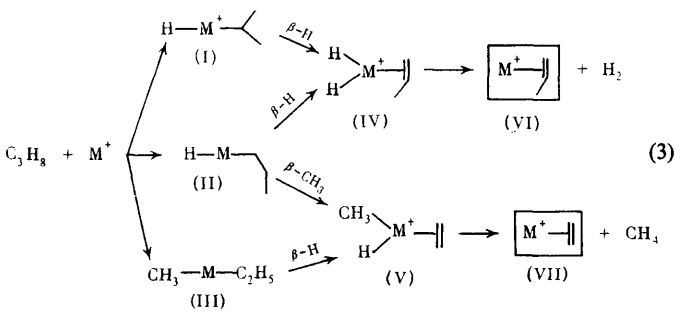
1. Cleavage of C–C bonds by metal ions in the gas phase

Alkanes and cycloalkanes can react with Fe^+, Ni^+, Co^+, Ta^+ and other ions in the gas phase.[75–92] The reactions are accompanied by cleavage of not only C–H but also C–C bonds. Furthermore, the cleavage of C–C bonds is frequently an exothermic process and constitutes the predominant conversion route of paraffins.

Examples of the cleavage of C–C bonds in alkanes and cycloalkanes by metal ions in the gas phase are given below (the observed reaction products are enclosed in boxes):



The proposed mechanism for the interaction of alkanes with Co^+, Ni^+, Fe^+, and other ions (for the reaction with propane) is shown in scheme (3):[86–89]

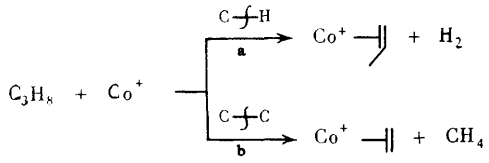


(3)

Scheme (3) involves the oxidative addition of C–H and C–C bonds of the alkane to M^+ to form intermediates (I), (II), and (III), the intramolecular transfer of β-H and β-CH_3 groups to the metal, resulting in the formation of dihydride (IV) and alkylhydride (V) olefin complexes, and elimination of H_2 from intermediate (IV) and CH_4 from intermediate (V) to give the observed olefin complexes (VI) and (VII).

Recently the reaction of alkanes with Co^+ and Ni^+ ions was made the subject of a more thorough investigation.[89] In this case an unusual feature of the reaction between propane and Co^+ was detected, which lay in the fact that of the two parallel reactions for cleavage of a C–H bond (4a) and a C–C bond (4b), the first predominates at low energies (0.1 eV) and the second predominates

at high energies (1 eV). The ratio of yields of $Co^+C_2H_4$:$Co^+C_3H_6$ was 1:2 in the first case and 3:1 in the second case.



(4)

Georgiadis et al.[89] assumes that cleavage of the C–C bond (4b) at a low energy occurs to a lesser degree because the overall reaction (4b) includes the endothermic elimination of methane from intermediate (V) [(V)→(VII) in scheme 3)], the energy barrier of which is 1.6 ± 0.7 kcal mol^{-1}. According to estimates, on going from methane to heavier homologues with the number of carbon atoms not less than 3, this barrier decreases from 19 to only a few kcal mol^{-1}. Since there is an endothermic stage, the overall exothermic‡ reaction (4b) [(II) or (III)→(V)→(VI) in scheme (3)] occurs with greater difficulty than reaction (4a), in which there is no endothermic stage [(I) or (II)→(IV)→(VI) in scheme (3)].

The two alternative mechanisms given in scheme (3) were examined[89] in order to explain why the C–C bond is preferentially cleaved as a result of the reaction between propane and Co^+ at high energies and also as a result of a wide range of reactions between alkanes and Ni^+, Fe^+, and Co^+ at all energies.

In accordance with the first mechanism, cleavage of the C–C bond occurs solely as a result of the insertion of M^+ into this bond [via intermediate (III)]. On the other hand, the transfer of the β-CH_3 group (III)→(V) does not occur. In this case the ratio of yields of products $M^+C_2H_4$:$M^+C_3H_6$ is determined completely by the ratio of probabilities of the oxidative addition of M^+ to the C–C and C–H bonds. The predominance of C–C clevage is due to thermodynamic factors—a weaker bond (compared to C–H) is broken and a stronger M^+–C bond (compared to M^+–H) is formed (Table 4).

The alternative mechanism is based on the assumption that both reactions for cleavage of the C–H and C–C bonds start with a common stage involving insertion of M^+ into C–H bonds. Insertion of M^+ into the C–C bond does not occur because of steric hindrance. The cleavage of the C–C bond occurs through the successive reactions (II)→(V)→(VII) [scheme (3)]. In this case preferential cleavage of the C–C bond may occur because transfer of the β-CH_3 group [(II)→(V)] predominates over transfer of β-H [(I) or (II)→(IV)] since formation of a stronger $M-CH_3$ bond is more favourable. In this case the ratio of $M^+C_2H_4$:$M^+C_3H_6$ or

$$C\text{–}C \,/\, C\text{–}H$$

must be equal to the ratio of the number of primary to secondary C–H bonds in propane, i.e., 3:1. This ratio actually occurs in the reaction of propane with Fe^+.[90] In the reaction of propane with Ni^+ the ratio of

$$C\text{–}C \,/\, C\text{–}H$$

increases to 3.5–4.0:1, which in the opinion of Schultz et al.,[90] could indicate a certain contribution from the mechanism for insertion of Ni^+ into a C–C bond. This reaction is exothermic, in contrast to the competing reaction for insertion of Ni^+ into a C–H bond (Table 4). Houriet et al.[91] have also shown that Ni^+ is mainly inserted into a C–C bond in reactions with linear alkanes.

Table 4. Energies of $M-CH_3$ and M–H bonds in the gas phase (kcal mol^{-1})*.

M	M+–H	M+–CH_2	M–H	M–CH_3
Ti	60	65		
Cr	35±4	37±7	—	—
Mn	53±3	71±7		
Fe	49.8±1.4	57.9	46±3	37±37
	53.2	54.6	38.7	34±9
Co	46.6±1.4	49.1±3.5	46±3	46±3
	51±5	61±4	39±6	41±10
	45.4	>56, <68	45±3	39.9
		57±7	42±3	
		46±14	54±10	
Ni	39.5±1.8	45.0±2.4	58±3	55±3
	41.9	41.3	62.1	53.7
	43±2	48±5	59±2	60
		<56	65±2	
			65±6	
Ru	41±3	54±5		
Rh	42±3	47±5	—	—
Pd	45±3	59±5		
Ta	54±5	65±5		

*The results of different authors cited in two studies[88,89] are summarised.

The ease of cleavage of the C–C bonds of alkanes by Fe^+, Ni^+, and Co^+ ions is due to the high energy of the M^+-CH_3 and $M-CH_3$ bonds in the gas phase. These energies are similar to the corresponding values of M^+–H and M–H and even exceed them (Table 4). Thus, the ratio of energies of these bonds in the gas phase is the opposite of what appears in solution. The difference in the strength of the bonds in the gas and condensed phases is attributed to the effect of steric factors in saturated systems (solution), resulting in a weakening of M–C bonds,[93] and also to the possibility of stabilisation of charge by the more polarisable alkyl group compared to H in ionic species in the gas phase.[83,86,89]

It should be emphasised that in all cases addition of a ligand to the metal inhibits cleavage of C–C bonds even in the gas phase. For example, replacement of Fe^+ by $Fe(CO)^+$ [77] and $Fe(CH_2)^+$ [84] is accompanied by a decrease in the proportion of C–C cleavage. The more shielded $Fe(CH_3)^+$ ion is completely inactive towards

‡ The energy of the $Co^+-C_2H_4$ bond (46 ± 8 kcal mol^{-1}) is 26 ± 8 kcal mol^{-1} greater than that needed for cleavage of the C–C bond.

aliphatic hydrocarbons.[85] In reactions of FeH^+, CoH^+, NiH^+, and $Co(CH_3)^+$ ions with alkanes only C–H bonds participate.[85,92] In contrast to the Ni^+ ion, the 14-electron complex $(\eta^5\text{-}C_5H_5)Ni^+$ does not cleave C–C bonds in hydrocarbons.[86]

Thus, the greater the steric hindrance, the lesser is the ability of the attacking species to cleave C–C bonds.

2. Cleavage of C–C bonds with small metal clusters

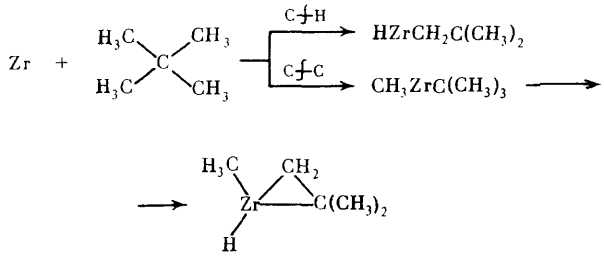
It was first shown in a study by Davis and Klabunde[91] that when atomic Ni and pentane are co-condensed at a low temperature very active small Ni clusters are formed, reacting with pentane even at −130 °C. In this case oxidative addition of the C–H and C–C bonds of the alkane to the Ni atoms occurs:

$$m\ Ni + n\ C_5H_{12} \xrightarrow{-196\,^\circ C} Ni_m(C_5H_{12})_n \xrightarrow[C\not\leftarrow H,\ C\not\leftarrow C]{-130\,^\circ C} \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!\diagdown\!\!(Ni)_m\!\!\diagup\!\!\begin{matrix} R^3 \\ R^4 \end{matrix}$$

R^1, R^2, R^3, R^4 = Alk, H.

The organic groups on the Ni atom inhibit the further agglomeration of clusters.

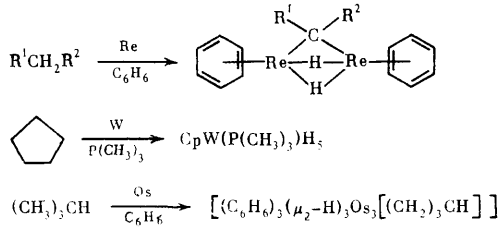
A similar pattern was observed in the co-condensation of Zr atoms with neopentane or isobutane.[95] Reaction of Zr with the alkane resulted in the formation of heterogeneous organozirconium surface complexes, to which Remick et al.[95] have attributed the following structure:



At the present time quite a few different examples of the vapour-phase synthesis of systems of a similar type are known.[96–101] They have various names in the literature: SMAD (Solvated Metal Atom Dispersion), obtained by dispersion of solvated metal atoms;[33,99–102] pseudo-organometallic powders;[33] ultradispersed metals;[103] ligand-free clusters;[103] metal microcrystals;[104] and others. In our opinion the most apt name is "low-ligand clusters",[105] reflecting the main characteristic of these systems.

Low-ligand clusters (LLCs) are intermediate between a compact metal and molecular clusters, being distinguished from both by the high percentage of surface atoms with low coordination numbers. In a bulk metal there are no ligand but the proportion of surface atoms is small while in molecular clusters all of the metal atoms are essentially saturated with ligands. The high percentage of surface atoms with low coordination numbers also governs the potentialities for using LLCs in catalysts, in particular for the cleavage of C–C bonds. The LLCs of nickel obtained by vapour-phase synthesis at normal temperatures are particles with a diameter of 25–36 Å or more (depending on the conditions of synthesis).[96] In terms of their catalytic activity they are superior to traditional Ni hydrocracking catalysts.[99,101] These systems can be used both in a pure form and in the form of particles deposited LLCs being the absence of a deactivating effect from the support.[102] The reasons for the increased activity of LLCs are discussed by Matsuo and Klabunde.[99] Bimetallic LLCs exhibit a particularly high activity.[100,101,106] For example, the presence in Co/SiO_2 of 2.5 at.% Mn–metal, which in itself is inactive in the hydrocracking of saturated hydrocarbons, increases the activity of the catalyst by a factor of 10^2.[100] It should be noted that the promotion of heterogeneous platinum catalyst with rhenium is widely used in industry.[107]

If the co-condensation of an atomic metal with an alkane takes place in the presence of a ligand [$P(CH_3)_3$, benzene], the reaction route changes considerably. In this case the conversions of alkanes take place solely with the participation of C–H bonds. On the other hand, the stabilising effect of the ligand hinders the agglomeration of the organometallic particle being formed. This method has been used for the synthesis of organometallic compounds:[108,109]



A serious disadvantage of the vapour-phase method for synthesising LLCs (in particular heavy metals, which are the most promising as catalysts) is the necessity to use special high-vacuum equipment. Therefore an attempt was made to synthesise catalysts for the cleavage of C–C bonds of alkanes based on LLCs by the conventional reduction of a transition metal compound in solution under conditions that excluded the deactivation of the LLC being formed.[105] It was shown that the reduction of OsO_4 in an alkane or arene with molecular hydrogen at 100–150 °C for 3–15 h or at 20 °C for 3 days resulted in the formation of active catalysts for the hydrocracking of paraffins:

$$OsO_4 + 4\,H_2 \xrightarrow[-4H_2O]{} \ll Os \gg \xrightarrow{RH} Os_{2.5-1.5}C_1H_{2-0}$$

An analysis of the EXAFS spectra showed that the pyrophoric osmium catalysts obtained in this way are actually Os LLCs with a particle diameter of 7–12 Å (if the synthesis is carried out at 20 °C) or 12–20 Å (at 150 °C). The combined data on hydrogenation and deuteration of the dry catalyst and other material suggest that the clusters are stabilised by carbon-containing ligands (probably CH_3, CH_2, CH, and C≡). It was established using EXAFS and XANES§ that for every surface Os atom there were 0.39–0.64 C atoms and the Os–C distance was 2.11–2.19 Å.[110]

The LLCs of Os obtained by a chemical method have similar properties to the LLCs of Ni and Co that are synthesised by a vapour-phase method (Table 5). The main product of the hydrogenation of all of these LLCs is methane.

Osmium LLCs have considerably higher activity than that of both cellular osmium and osmium black. The latter even at 180 °C is appreciably less active than osmium LLCs at 100 °C. At the same time fine LLCs (10 Å) exhibit higher activity than the coarser forms.[105] Hydrocracking of alkanes and cycloalkanes in the

§ X-Ray Absorption Near-Edge Structure.

presence of osmium LLCs takes place effectively at 100–150 °C at an initial H_2 pressure of 50 atm. Under these conditions 1 mole of catalyst has converted hundreds of moles of hydrocarbon after 5–15 h, and the catalyst can be used repeatedly without loss of activity.

Table 5. Certain properties of LLCs of osmium,[105] nickel, and cobalt[96].

LLC	Overall composition	Specific surface $m^2 g^{-1}$	Particle size, Å
Os (20° C)*	$Os_{1,5}CH_{0-2}$	34	7–12
Os (150° C)*	$Os_{2,3-2,5}CH_{0-2}$	46	12–20
Ni**	$Ni_{2-9}CH_{2-3}$	37–40	25–36
Co**	Co_4CH_2	—	18–21

* Obtained by chemical synthesis.
** Obtained by gas-phase synthesis.

We can illustrate the composition of the products from the hydrocracking of certain alkanes and cycloalkanes (in moles per mole of converted RH) on osmium (LLCs) with a particle size of 10 Å (Os-I) and 20 Å (Os-II) (initial H_2 pressure 50 atm., reaction time 15 h):[105]

$$n\text{-}C_5H_{12} + H_2 \xrightarrow[89\%\ \text{conversion of RH}]{\text{Os-I, 120° C}} \underset{0.06}{C_4} + \underset{0.31}{C_3} + \underset{0.71}{C_2} + \underset{2.20}{C_1}$$

$$n\text{-}C_6H_{14} + H_2 \xrightarrow[60\%]{\text{Os-II, 150°}} \underset{0.10}{C_5} + \underset{0.04}{C_4} + \underset{0.11}{C_3} + \underset{0.50}{C_2} + \underset{3.29}{C_1}$$

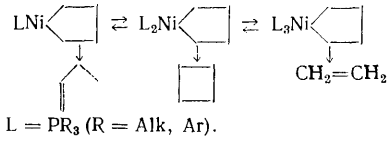
$$cyclo\text{-}C_5H_{10} + H_2 \xrightarrow[94\%]{\text{Os-II, 120° C}} \underset{0.88}{C_5} + \underset{0.04}{C_4} + \underset{0.07}{C_3} + \underset{0.09}{C_2} + \underset{0.22}{C_1}$$

$$cyclo\text{-}C_6H_{12} + H_2 \xrightarrow[89\%]{\text{Os-II, 150°C}} \underset{0.25}{C_6} + \underset{0.10}{C_5} + \underset{0.11}{C_4} + \underset{0.14}{C_3} + \underset{0.24}{C_2} + \underset{0.44}{C_1}$$

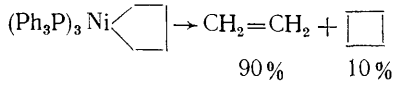
The conversion products of n-alkanes containing 5, 6, 8, or 18 carbon atoms (120–150 °C, 15 h) are represented by the complete range of lower alkanes from C_1 to C_{n-1}, with 80–97% of this being made up as a rule by methane, ethane, and propane. All of the products of cracking of n-alkanes have a linear structure. Cyclopentane and methylcyclopentane undergo hydrogenolysis to an appreciable extent at 100 °C. At 100–120 °C the hydrogenolysis of cyclopentane is effective and takes place selectivity to give n-pentane—a product of ring-opening. Selective opening of the ring also occurs in methylcyclopentane with cleavage of the least shielded bonds and formation of 2- and 3-methylpentanes.

3. Cleavage of C–C bonds in alkyl complexes of transition metals

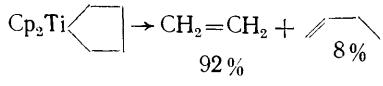
By assuming that C–C bonds are cleaved in intermediate alkyl complexes of transition metals in the gas phase (see Section II), it is possible effectively to elucidate the large quantity of experimental material on the reactions of alkanes and cycloalkanes with metal ions. The reactions of this type could be observed directly in solution. Thus, phosphine complexes of nickel metallocyclopentanes undergo reductive elimination, β-hydride elimination, and C–C cleavage.[111] The contribution of each of these processes depends on the coordination number of the Ni atom:



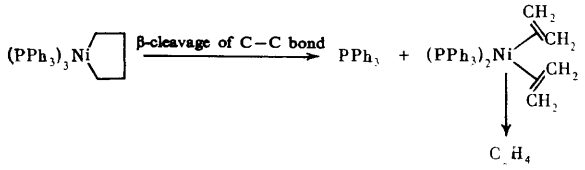
The Ni triphenylphosphine complex with the highest coordination number decomposes to form ethylene and cyclobutane;



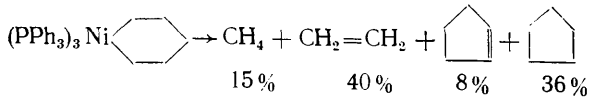
Ethylene is also formed as the main product from a titanocyclopentane complex:



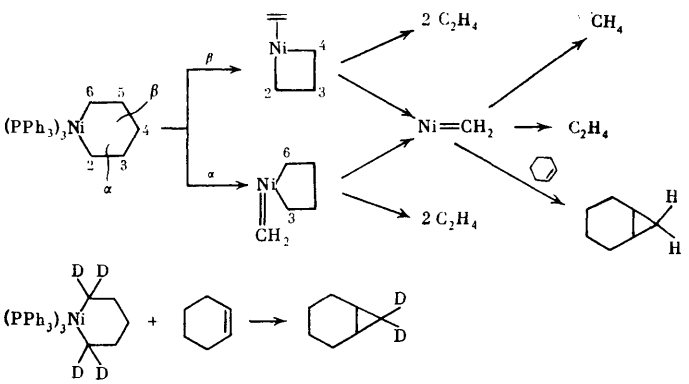
In both cases reaction takes place with the formation of intermediate bis(ethylene) complexes:[112]



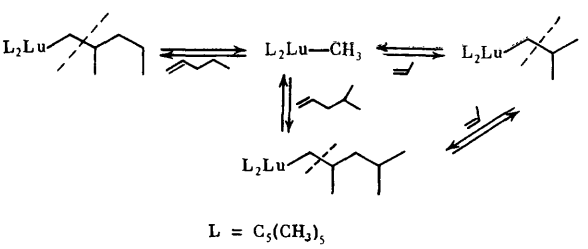
Cleavage of C–C bonds also occurred in Ni-cyclohexane:[111]



It was possible to demonstrate using complexes labelled with deuterium and with the use of traps (cyclohexene) that of the two possible routes for cleavage of C–C bonds α-elimination predominates.

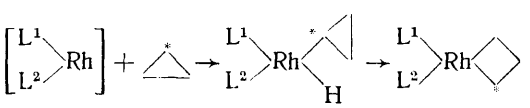


The β-cleavage [sic] of C–C bonds was observed in lutetium alkyl complexes.[113] In this case the cleavage and formation of C–C bonds are reversible:



These reactions, which take place in solution, represent the α- and β-cleavage of C–C bonds in alkyl complexes of transition metals. The proposed cleavage of C–C bonds according to scheme (2b) is thus confirmed experimentally.

Another form of cleavage of a C–C bond in a Rh cyclopropyl derivative has also been reported:[56]

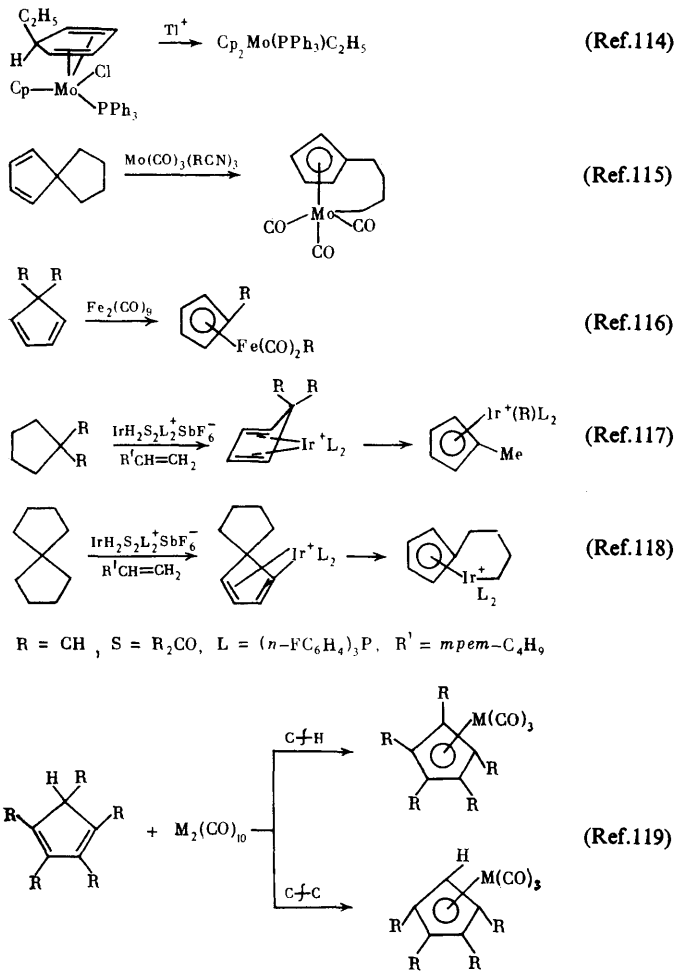


$L^1 = C_5(CH_3)_5$, $L^2 = P(CH_3)_3$.

4. Stoichiometric cleavage of C–C σ-bonds in hydrocarbons by transition metal complexes in solution

Because the cleavage of C–C bonds in alkanes by an attacking species is severely inhibited when steric hindrance increases, cases of the cleavage of single C–C bonds by transition metal complexes (even stoichiometric reactions) are extemely rare.

Examples of such reactions[114–119] are given below:



(Ref.114)

(Ref.115)

(Ref.116)

(Ref.117)

(Ref.118)

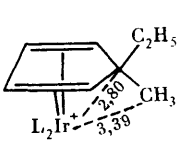
R = CH, S = R_2CO, L = $(n\text{-}FC_6H_4)_3P$, R' = *mpem*-C_4H_9

(Ref.119)

R = CH_3, when M = Mn
when M = Re the C–C bond is not cleaved.

In these examples, as in other similar reactions, the driving force of the reaction is formation of the π-complex of a cyclopentadienyl aromatic system, which provides an additional energy gain of 25 kcal mol^{-1}.

It is interesting that an agostic C–C bond was first detected[18] in the complex



The reactions of alkanes and cycloalkanes with carbonyl and carbonylhydride clusters of osmium and iridium, "bare" clusters of bismuth, and other clusters[120] have also been studied. In all cases

cleavage of a C–C bond in RH ny ML_n at 180 °C was found not to occur

$$RH \xrightarrow{ML_n,\ 180^\circ C} \gtrless C\text{–}C \lesssim \quad \text{does not occur}$$

RH = n-C_6H_{14}, cyclo-C_5H_{10}, cyclo-C_5H_9R, cyclo-C_6H_{12} etc.,

ML_n = $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, $H_2Os_3(CO)_{12}$, Bi_4^{2-}, Bi_5^{3-} etc.

Muetterties came to the conclusion that the use of metal carbonyl clusters in reactions involving aliphatic hydrocarbons had no future potential.[120]

Table 6. Logarithms of equilibrium constants of the hydrocracking reactions of alkanes and cycloalkanes calculated from the data of Zhorov[45].

Reaction	K_p, at T, K		
	300	500	700
$C_6H_6+H_2 \rightleftarrows 2CH_4$	11.971	7.472	4.359
$C_6H_{14}+H_2 \rightleftarrows CH_4+C_5H_{12}$	10.267	6.399	4.634
$C_8H_{18}+H_2 \rightleftarrows C_2H_6+C_6H_{14}$	8.637	5.483	4.008
cyclo-$C_5H_{10}+H_2 \rightleftarrows C_5H_{12}$	7.157	3.374	1.341
cyclo-$C_6H_{12}+H_2 \rightleftarrows C_6H_{14}$	5.560	2.520	1.207

One report[121] states that the fragmentation of alkanes on exposure to γ-radiation is inhibited in the presence of $Co_2(CO)_8$ and at the same time there is the formation of $Co_3(CO)_9CR$ complexes, where R = CH_3, C_2H_5, and $CH(CH_3)_3$.

5. Catalytic cleavage of C–C bonds in alkanes and cycloalkanes by Ziegler-type systems

By taking into account the considerably steric shielding of the carbon atoms of a C–C bond, Akhrem et al.[122,123] formulated the requirements which must be satisfied by transition metal complexes that are capable of activating and cleaving such bonds:

a) the transition metal–carbon bond energy must be fairly high, which on the whole is typical for metals of the higher periods;

b) the degree of oxidation of the metal must be low, in other words, the metal must be capable of undergoing oxidative addition with ease;

c) the complex must have a low coordination number, which ensures the minimum steric hindrance in attack on the C–C bond;

d) ligands of a small size must be present on the metal atom, giving rise to the minimum steric hindrance (for example, H and CO).

Since conditions a–d will be conductive to activation of not only C–C bonds but also the more reactive C–H bonds, a shift in the equilibrium towards cleavage of C–C bonds according to scheme (5) could be assisted by inclusion into the reaction sphere of an additional reagent that reacts irreversible with the product of

Table 7. Hydrogenolysis of saturated hydrocarbons by systems based on rhenium carbonyl complexes and organoaluminium compounds[122].

RH	Catalyst[a]	RH : AlR_3 : Re_mL_n, mol	T, °C	Time, h	Conversion of RH		Products[b], mol per mol of reacted RH						
					%	mol per mol of Re_mL_n	C_1	C_2	C_3	C_4	C_5	C_6	C_7
C_6H_{14}	$Re_2(CO)_{10}$+A	100:6:1	180	3	77	77	2.81	0.53	0.28	0.17	0.16	—	—
C_6H_{14}	$Re_2(CO)_{10}$+A	100:6:1	150	3	16	16	1.39	0.28	0.15	0.21	0.57	—	—
C_8H_{18}	$Re_2(CO)_{10}$+A	100:6:1	180	5	65	65	1.56	0.30	0.16	0.16	0.18	0.18	0.22
C_8H_{18}	$Re_2(CO)_{10}$+B	190:10:1	180	15	48	91	2.00	0.46[c]	0.11	0.15	0.16	0.18	0.27
cyclo-C_5H_{10}	$Re_2(CO)_{10}$+A	100:6:1	180	3	93	93	0.89	0.17	0.11	0.16	0.43	—	—
cyclo-C_5H_{10}	$Re_2(CO)_{10}$+A	100:6:1	150	5	27	27	0.11	0.02	0.02	0.08	0.83	—	—
cyclo-C_5H_{10}	$Re_2(CO)_{10}$+A	100:9:1	180	15	94	94	0.61	0.12	0.08	0.14	0.46	—	—
cyclo-C_5H_{10}	$Re_4H_4(CO)_{12}$+A	200:12:1	180	15	84	168	0.98	0.16	0.13	0.07	0.58	—	—
cyclo-$C_5H_9CH_3$	$Re_4H_4(CO)_{12}$+A	200:12:1	180	15	82	164	0.94	0.10	0.04	0.07	0.19	0.50	—
cyclo-$C_5H_9CH_3$	$Re_3H_3(CO)_{12}$+A	200:9:1	180	15	82	164	1.14	0.12	0.04	0.08	0.18	0.40	—
cyclo-C_6H_{12}	$Re_2(CO)_{10}$+A	100:6:1	180	3	22	22	0.85	0.11	0.05	0.09	0.22	0.30	—
cyclo-$C_{10}H_{20}$	$Re_2(CO)_{10}$+B	26:9:1	180	15	78	21	0.93	0.69[c]	0.06	0.06	0.05	0.04	0.04[d]

[a] A = iso-$(C_4H_9)_2AlH$, B = $(C_2H_5)_3Al$; [b] n-alkanes in every case except those marked with an asterisk; [c] $(C_2H_5)_3Al$ is a source of ethane in addition to the hydrocarbon; [d] C_8 (0.06), C_9 (0.14), and C_{10} (0.14) alkanes are also formed.

insertion of the metal complex into this bond. This type of reagent could be, for example, hydrogen:

$$\begin{array}{c} RCH_2CH_2{-}M{-}H \rightleftarrows RCH_2CH_3 + M \rightleftarrows RCH_2{-}M{-}CH_3 \\ \downarrow H_2 \qquad\qquad\qquad\qquad\qquad\qquad \downarrow H_2 \\ RCH_2{-}CH_3 + MH_2 \rightleftarrows M + H_2 + RC_2H_5 \; RCH_3 + CH_4 + MH_2 \end{array} \quad (5)$$

It is significant also that the hydrocracking of saturated hydrocarbons is a thermodynamically favourable reaction (especially at lower temperatures, see Table 6).

Thus, the problem could be stated as follows: to study the possibility of cracking paraffins with H_2 on catalysts which meet conditions a–d.

An experiment with a number of compounds of different transition metals, mainly from Groups VI–VIII (carbonyls, carbonylhydrides, oxides, halides) and systems based on them, showed that the rhenium carbonyl and carbonylhydride complexes $Re_2(CO)_{10}$, $Re_3H_3(CO)_{12}$, $Re_4H_4(CO)_{12}$ in combination with organoaluminium compounds [$Al(C_2H_5)_3$, $(iso\text{-}C_4H_9)_2AlH$] are actually capable of activating C–C bonds in alkanes and cycloalkanes such as hexane, octane, cyclopentane, methylcyclopentane, cyclohexane, and others, and of catalysing their hydrogenolysis. The reactions occur in the respective hydrocarbon at 150–180 °C and at an initial H_2 pressure of 50 atm. At 180 °C after several hours a conversion close to quantitative is achieved, 1 mole of rhenium compound catalysing the conversion of hundreds of moles of hydrocarbons (Table 7).

The activity of the catalytic system depends to a considerable extent on the ratio of the components. Thus, the activity of the catalyst formed by interaction of $Re_2(CO)_{10}$ with $(iso\text{-}C_4H_9)_2AlH$ reaches a maximum at an atomic ratio of Al : Re = 3 : 1, with an increase of this ratio to 5.5 : 1 or a decrease to 1.5 : 1 leading to complete loss of activity.

The catalyst remaining after removal of the gaseous and liquid reaction products retains its activity and can cause subsequent batches of hydrocarbon to undergo hydrogenolysis. Organoaluminium compounds used separately, in the same way as rhenium complexes [$Re_2(CO)_{10}$, $Re_3H_3(CO)_{12}$, $Re_4H_4(CO)_{12}$, $CpRe(CO)_3$, Na_2ReH_9, Na_2ReH_9 + 18-crown-6] in the absence of organoaluminium compounds, do not have any hydrocracking activity towards alkanes (the reaction was carried out at 180 °C for 40 h.[122,123]

The main conversion products of n-alkanes at the early stages of the reaction are methane and linear hydrocarbons that contain one carbon atom less than in the original paraffin. Thus, in paraffins initially it is mainly the terminal CH_2-CH_3 bonds that are cleaved:

$$R{-}CH_2CH_3 + H_2 \xrightarrow{[Re]} RCH_3 + CH_4$$
$$\downarrow [Re]H_2$$
$$C_1 + C_2 + C_3 + \text{etc.}$$

The primary products of the hydrocracking of unsubstituted cycloalkanes are mainly linear alkanes with the same number of carbon atoms:

$$\underset{(CH_2)_n}{\bigcirc} + H_2 \xrightarrow{[Re]} H{-}(CH_2)_n{-}H$$
$$\downarrow [Re]H_2$$
$$C_1 + C_2 + C_3 + \ldots \text{ etc.}$$

Also, in the conversion products of alkanes and cycloalkanes lower hydrocarbons formed through subsequent multistage hydrogenolysis are always present. The proportion of these increases with an increase in conversion of the initial paraffin.

The catalysts are X-ray-amorphous insoluble pyrophoric powders containing Re (70%), Al (16%), C (4–9%), and H (1–2%). Hydrogenation of the catalysts with hydrogen at 100–200 °C or protolysis of them (using aqueous H_2SO_4 and CH_3COOH) leads to the isolation of C_1-C_5 alkanes (mainly C_4-C_5).

In the IR spectra of the catalysts two weak absorption bands occur at 1900 and 2025 cm^{-1}, which are attributed to Re–H bond vibrations. Analysis of the EXAFS spectra of the L_{III} region of rhenium showed that each rhenium atom is bound to 2–3 carbon atoms (Re–C distance is equal to 2.18 Å) and to 1–2 metal atoms (Re–M bond length is 2.6–2.7 Å, M = Re or Al). Thus, there is reason to believe that the catalytic systems obtained are organometallic rhenium hydride complexes.[122,123]

III. Novel superacid complexes — effective reagents and catalysts of low-temperature conversions of alkanes and cycloalkanes

The basicity of alkanes is low and therefore the rate of their conversions by even strong proton and aprotic acids at 20 °C is extremely slow.[43,44,124–126]

In our research into effective electrophilic catalysts for conversions of paraffins we turned our attention to the well-known Friedel–Crafts complexes $RCOX.AlX_3$.[127–132] At room temperature, in the same way as aluminium halides, they are inactive in reactions with alkanes.[124] However, a molecule of acid chloride contains two potentially nucleophilic sites X–C(R)=O and only one of these participates in the formation of an $RCOX.AlX_3$ complex. It has transpired that addition of a further mole of AlX_3 to traditional $RCOX.AlX_3$ systems causes a rapid change in their properties, converting complexes that are inert towards paraffins into very active reagents which have higher reactivity than not only Lewis acids and systems based on them but also, as a rule, the strongest proton superacids. Complexes of this type have been called aprotic organic superacids (AOS).[27,28,133]

1. Cracking of n-alkanes

$RCOX.2AlX_2$ complexes (R = CH_3, R = C_3H_7, X = Br, Cl) react extremely readily with C_5-C_{18} n-alkanes. In this case the latter undergo cracking to form the same principal products.[133,134]

$$C_nH_{2n+2} \xrightarrow{RCOX_2AlX_2} iso\text{-}C_4H_{10} + iso\text{-}C_5H_{12} + iso\text{-}C_4H_9COR +$$
$$+ iso\text{-}C_4H_7COR + \text{oligomer}$$

For alkanes with *n* ranging from 5 to 18 conversion reaches 100% after 30 min at 20 °C. The resulting oligomers are branched polyunsaturated hydrocarbons with a molecular weight of 700–800.

Isobutane, isopentane, and oligomeric products are also formed when alkanes are treated with other catalysts based on aluminium halides, but these reactions occur under quite different conditions.[124–126]

The rate of catalytic cracking of n-alkanes in solution is especially high. Thus, in the presence of the complex $CH_3COBr.2AlBr_3$ (VIII) in CH_2Br_2 the conversions of C_8-C_{18} alkanes to cracked products

at room temperature reach 70–85% after only 10 min, and in the presence of the complex $CH_3COX.2AlCl_3$ (IX) there is 57–70% conversion after 20 min (Figs. 1 and 2). Such high rates of cracking do not occur even when the most active proton superacid systems are used, so that AOS, and primarily (VIII), can be classed as one of the most active catalysts for the fragmentation of n-alkanes. However, the number of catalytic cycles does not exceed 15 and decreases with an increase in length of the carbon chain of the alkane. Cyclododecane behaves similarly towards $RCOX.2AlX_3$ complexes. At room temperature it is cracked very readily to give the same principal products.

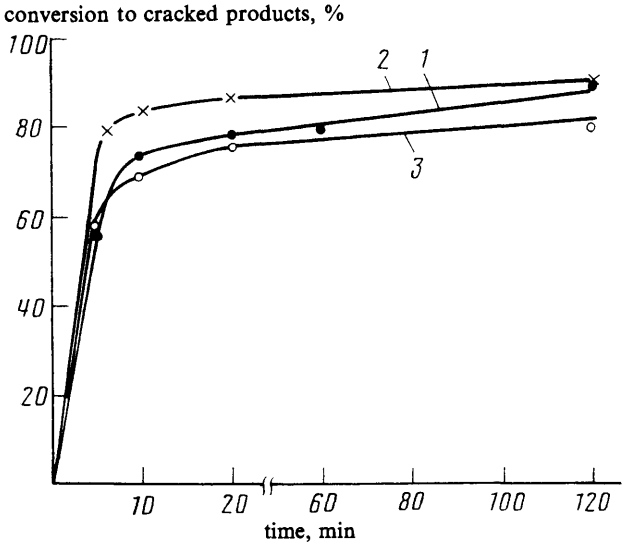
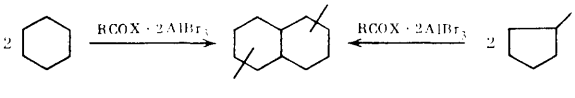


Figure 1. Cracking of C_8–C_{18} n-alkanes by the complex $CH_3COBr.2AlBr_3$ in CH_2Br_2 solution (20 °C, $[CH_3COBr]$ = 0.20 mol litre^{-1}) at the following ratios: *1*, $C_8H_{18}:CH_3COBr.2AlBr_3$ = 10:1; *2*, $C_{12}H_{26}:CH_3COBr.2AlBr_3$ = 5:1; *3*, $C_{18}H_{38}:CH_3COBr.2AlBr_3$ = 3:1.[133]

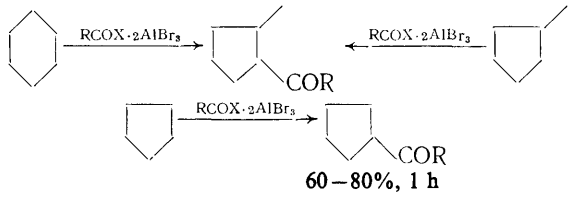
2. Oxidative combination and acylation of C_5–C_6 cycloalkanes

Aprotic organic superacids readily react with five- and six-membered cycloalkanes at 20 °C and lower temperatures.[27] The reactions occur by one of the three routes indicated below, and in certain cases the product yields are quite high. When there is excess cycloalkanes and in the absence of a solvent, cyclohexane or methylcyclopentane undergo oxidative coupling to form dimethyldecalins (mainly the 2,6- and 2,7-isomers):

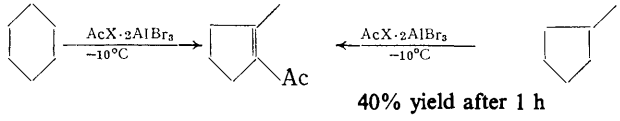


[the ratio of RH:(VIII) = 12:1; at 20 °C conversion is 100% after 1 h]. An increase in the concentration of electrophilic reagent suppresses this process and favours the acylation of cycloalkanes.

Acylation is the sole route for cyclopentane under all conditions.



On increasing further the concentration of acylating agent, namely, when it is in excess, when the temperature is lowered dehydroacylation of cyclohexane or methylcyclopentane can be achieved:



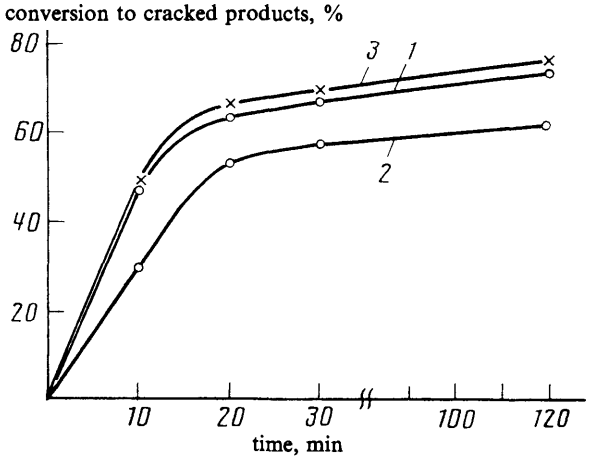


Figure 2. Cracking of C_8–C_{18} n-alkanes by the complex $CH_3COBr.2AlBr_3$ in CH_2Br_2 solution (20 °C, $[CH_3COBr]$ = 0.43 mol litre^{-1}) at the following ratios: *1*, $C_8H_{18}:CH_3COBr.2AlBr_3$ = 10:1; *2*, $C_{12}H_{26}:CH_3COBr.2AlBr_3$ = 5:1; *3*, $C_{18}H_{38}:CH_3COBr.2AlBr_3$ = 3:1.[133]

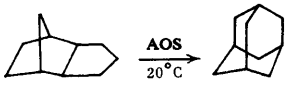
3. Isomerisation of C_4–C_6 n-alkanes to isoalkanes and saturated tricyclanes to adamantane and its homologues

Complex (VIII) catalyses the isomerisation of n-butane to isobutane at 20 °C.[134,135] At a ratio of n-C_4H_{10}:(VIII) = 11:1 the equilibrium concentration of isobutane is reached within 3 h, the selectivity of isomerisation being 90% (at the earlier stages it is about 100%). In terms of activity complex (VIII) has no equal amongst all of the known catalysts for the isomerisation of n-butane, including the strongest proton superacids. Complex (IX), although less active than (VIII), is also more active than known catalysts based on AlX_3.

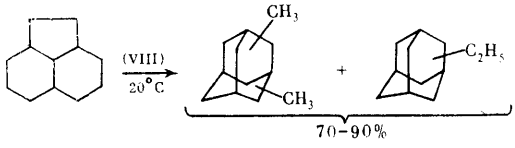
In contrast to higher alkanes, the cracking of n-pentane and n-hexane by aprotic organic superacids in CH_2Br_2 has an induction period during which there is a rapid and selective isomerisation of

n-pentane to 2-methylbutane, while n-hexane is isomerised to a mixture of all four possible isohexanes.[136] The yields of isoalkanes in the presence of (VIII) and (IX) reach 55–75% after 15–60 min and 50–60% after 90–120 min respectively with an almost complete absence of fragmentation.

Aprotic organic superacids effectively catalyse the synthesis of adamantane and its derivatives from isomeric saturated tricyclanes. Thus, they initiate the isomerisation of trimethylenenorbornane to adamantane:[13]

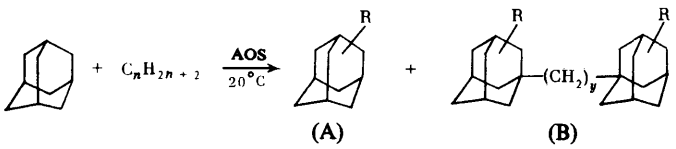


Complex (VIII) is also the most effective of all the known catalysts for isomerisation of perhydroacenaphthene or its isomeric $C_{12}H_{20}$ tricyclanes to a mixture of dimethyl- and ethyl-adamantanes in which 1-ethyladamantane predominates.[137] At 20 °C the initial hydrocarbons have already undergone quantitative conversion after only 5–12 min.



4. Alkylation of adamantane with n-alkanes

Alkylation of adamantane (AdH) with n-alkanes is a promising method for obtaining alkyladamantanes (AdAlk), whose use in the form of individual compounds or mixtures is of considerable interest.[138] The known methods for the alkylation of AdH are not very effective and are not at all suitable for the synthesis of higher AdAlk.[138–141] It was recently found that n-alkanes very readily alkylate AdH in the presence of AOS at 20 °C.[134,142] When stoichiometric quantities of complexes are used the conversion of AdH has reached 90–100% after 20 min. Under catalytic conditions [(AdH : (VIII)] = 8 : 1] the reactions with C_8–C_{18} alkanes are complete within 3 h, the total yield of AdAlk being 110–220 wt.% based on adamantane. The reaction products mainly comprise two types of compound—(A), which has a single adamantane ring with a total number of carbon atoms m ranging from 11 to 33, and (B) from m ranging from 23 to 51.



$n = 6–18$; R—one or more groups

In addition to the high rates of alkylation and yields of AdAlk, the possibility of regulating the composition of the resulting mixture with respect to the content of higher and lower homologues and the ratio of mono- to poly-AdAlk should also be included amongst the merits of this method.

5. Functionalisation of alkanes and cycloalkanes

The single-state functionalisation of paraffins is a promising method for the direct synthesis of organic compounds based on readily available hydrocarbon feedstocks.[14,15] Complexes (VIII) and (IX) effectively catalyse the ionic bromination of C_4–C_7 n-alkanes, cyclopentane, cyclohexane, trimethylenenorbornane, and other compounds at −20 and +20 °C to give exclusively or principally monobromides in high yield—55–370 wt.% based on complex (IX) and 110–910 wt.% based on (VIII).[143]

$$RH + Br_2 \rightarrow RBr + HBr.$$

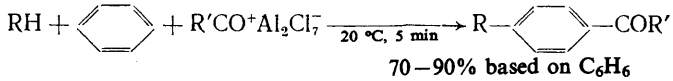
The maximum yield of RBr based on Br_2 is 75%, bromination is not complicated by fragmentation. The monobromides that are formed from alkanes comprise mixtures of isomers; pure alkylcyclobromides are formed from cyclohexane and cyclopentane, which may be of interest synthetically. Until the study of Akhrem et al. was published,[143] the ionic bromination of n-alkanes had not been reported, while for simple iso- and cyclo-alkanes it was ineffective.[144,145]

The considerable potentialities of AOS are indicated by other reactions for the functionalisation of alkanes which take place in their presence. One of these is the single-stage synthesis of organosulphur compounds from alkanes (or cycloalkanes) and elemental sulphur:

$$RH + S + R'CO^+Al_2X_7^- \xrightarrow[0-20\ ^\circ C]{} \underset{25-60\,\%}{\text{sec-RSCOR'}}$$

$RH = C_3H_8$, n-C_4H_{10}, n-C_5H_{12}, cyclo-C_5H_{10}, cyclo-C_6H_{12};
$R' = CH_3$, C_3H_7, Ph.

Another example is the alkylation and acylation of benzene in a single stage to form alkylated aromatic ketones. Isoalkanes and cycloalkanes with a tertiary carbon atom act as alkylating agents:



70–90% based on C_6H_6

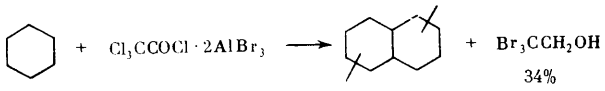
RH = iso-C_4H_{10}, iso-C_5H_{12}, iso-C_6H_{14}, cyclo-$C_6H_{11}CH_3$.

6. Saturated hydrocarbons as reducing agents of acyl halides in the presence of $AlBr_3$

In the reactions between $RCOX.2AlX_3$ complexes and saturated hydrocarbons the latter act as reducing agents, initially converting the acyl halides which form part of these complexes into aldehydes:

$$RH + R'COX \cdot 2\,AlX_3 \rightarrow R^+ \ldots\ Al_2X_7^- + R'COH.$$

Examples of the reduction of acyl halides by saturated hydrocarbons in the presence of aluminium halides (20 °C, 1 h) are given below. In certain cases halogen exchange occurs in parallel with reduction.[134,146]



$$AdH + PhCOCl \cdot 2\,AlBr_3 \rightarrow \underset{70\,\%}{1\text{-Br-Ad}} + \underset{82\,\%}{PhCHO} + 2\,AlBr_3,$$

$$ClCO(CH_2)_3COCl + RH \xrightarrow[2)\ H_2O/H^+]{1)\ AlBr_3} \underset{40\,\%}{BrCH_2CH(Br)CH_2CH_2COH}.$$

7. Nature of the superacidic properties of $RCOX.2AlX_3$ complexes

With the aim of trying to account for the unusually high activity of $RCOX.2AlX_3$ complexes, which clearly distinguishes them from the well established $RCOX.AlX_3$ complexes, the structure of $RCOX.2AlX_3$ complexes (VIII) and (IX) and $RCOX.AlX_3$ complexes (X) were studied in the solid state and solution using NQR, ^1H, ^{13}C, ^{27}Al, and ^{17}O NMR and vibrational spectroscopy.[134,147,148] It was established that in the solid state they all comprise ionic acylium salts which differ only according to the structure of the anion: $RCO^+Al_2X_7^-$ for (VIII) and $RCO^+AlX_4^-$ for (X). In solution (CH_2X_2) (VIII) and (IX) consist of equilibrium mixtures of acylium salts $RCO^+Al_2X_7^-$ and donor-acceptor complexes $RC(X)=O\rightarrow Al_2X_6$, while complexes (X) exist solely in the form of coordination complexes $RC(X)=O\rightarrow AlX_3$:

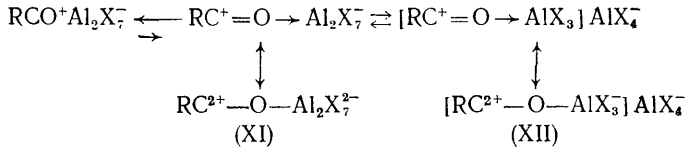
$$RCOX + 2\,AlX_3 \rightarrow \underset{\text{in } CH_2X_2 \text{ solution}}{RC(X)=O\rightarrow Al_2X_6} \rightleftarrows RCO^+Al_2X_7^-,$$

$$RCOX + AlX_3 \rightarrow RC(X)=O\rightarrow AlX_3 \rightleftarrows RCO^+AlX_4^-.$$

In order to answer the question as to whether any acylium salt being generated in solution is capable of reacting at 20 °C with paraffins or whether the activity of the $RCO^+Al_2X_7^-$ acylium complexes is due to the presence of the dimeric anion forming part of its structure, it was necessary to synthesise two acylium salts that differed only according to the anion (one with a monomeric anion and the other with a dimeric anion) and to compare their reactivity. This problem was resolved in the case of two pairs of complexes: 1) $AcF.SbF_5$ and $AcF.2SbF_5$ (forming the acylium salts $Ac^+ScF_6^-$ and $Ac^+Sb_2F_{11}^-$ respectively in SO_2 solution); and 2) $MesCOBr.AlBr_3$ and $MesCOBr.2AlBr_3$ [which exist in CH_2Br_2 exclusively in the form of the ionic salts $MesCO^+AlBr_4^-$ and $MesCO^+Al_2Br_7^-$ respectively, Mes = 2,4,6-$(CH_3)_3C_6H_2$].[134,149] Only acylium salts containing a dimeric anion exhibited superacidic properties in reactions with alkanes and cycloalkanes while acylium salts with a monomeric anion were inactive at 20 °C.

Is it possible to relate such a marked difference in activity of $RCO^+AlBr_4^-$ and $RCO^+Al_2Br_7^-$ salts with the different degree of electrophilicity of the acylium cations in them? On the one hand it is true that the nucleophilicity of the $AlBr_4^-$ anion is greater than that of the $Al_2Br_7^-$ anion.[150] On the other hand, a substantial difference in the reactivity of these salts should be accompanied by an appreciable difference in the ^{13}C NMR spectra, which are very sensitive to a change in electron density. However, the ^{13}C NMR spectra of these salts are virtually identical, which raises doubts about the theory of the different electrophilicity of the acylium cations bound to monomeric and dimeric anions.[134,149]

The idea that in solutions of $RCO^+Al_2X_7^-$ complexes an equilibrium that is very much shifted to the left exists between the acylium salts and more electrophilic complexes in which the RCO^+ cations are coordinated with a Lewis acid deserves serious consideration.[149] It is clear that this type of coordination should lead to the formation of more electrophilic cations, which in the limiting case can be represented as acylium dications with the structures (XI) or (XII):



The latter probably exist in very low concentrations and cannot be identified by conventional spectroscopic methods, but it is they that are very likely to be responsible for the unusually high activity of $RCO.2AlX_3$ complexes—aprotic organic superacids.[149]

The idea that acyl halide complexes with two moles of AlX_3 of the type $RC(X\rightarrow AlX_3)=O\rightarrow AlX_3$ played an important part in the acylation of arenes was first suggested in 1962.[151] A report was recently published[152] stating that it was possible to detect the formation of the complex $CH_3C(Cl\rightarrow AlCl_3)=O\rightarrow AlCl_3$ in the system $AcCl-n$ moles of $AlCl_3$ in SO_2 solution using NMR. However, the interpretation of the spectroscopic data made in this study is at variance with that generally accepted and appears to be erroneous. Thus is has so far not been possible to observe complexes of the type (XI) or (XII) experimentally.

There would appear to be a direct analogy between complexes of the type (XI) or (XII) and the protosolvated form of the acylium cation (XIII), which was postulated by Olah et al.[153] as being formed in a proton superacid. Olah et al. assume that it is the protosolvated acylium cations (XIII) which are responsible for the transfer of a hydride ion from isobutane to the acylium cation that occurs in a proton superacid. In an aprotic solvent (SO_2) where ion (XIII) cannot be formed, the transfer of hydride ion from isobutane does not occur:

$$\underset{\text{(XIII)}}{CH_3C^+=O + H^+ \rightarrow CH_3C^+=O^+H},$$

$$\text{iso-}RH + CH_3C^+=O^+H \rightarrow \text{iso-}R^+ + CH_3CH=O^+H,$$

$$\text{iso-}RH + CH_3C^+=O \xrightarrow{SO_2} \text{iso-}R^+ + CH_3CHO.$$

Proton solvation of cations which contain atoms with a free electron pair is quite a general phenomenon.[154–156] The formation of the dications H_4O^{2+} and H_4S^{2+} was recently reported.[155,156]

In mentioning the similarity between postulated complexes of the type (XI) or (XII) and the protosolvated form of the acetylium cation (XIII), we should draw attention to the considerably greater activity of the former. Complexes of the type (XIII) are inert towards n-alkanes,[157,158] whereas $RCOX.2AlX_3$ systems react with them at high rates. Therefore, the possible presence of small quantities of protonated compounds in $RCOX.2AlX_3$ systems (from

traces of water or the destruction of complexes) cannot be the reason for the high activity of these systems, i.e., they should actually be regarded as aprotic organic superacids.

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During the last 20 years the term "paraffins" has progressively lost its original meaning.

Metal-complex activation of inert σ-bonds (H−H, Si−H, Si−C, C−H) has provided a powerful stimulus for the development of the chemistry of inert molecules. At the present time there is the problem of the metal-complex activity of C−C bonds in alkanes. Although up to the present time there has been no single example of the cleavage of such bonds on well-characterised transition metal complexes, the data given in this review in conjunction with the preliminary results obtained on Ziegler-type systems would appear to suggest the possible occurrence of such reactions.

The development of "low-temperature" reagents and catalysts for the conversion of unactivated saturated hydrocarbons seems to indicate the considerable unexhausted possibilities in this area. There is future potential in the development of chemical methods for the synthesis of active catalysts for the cleavage of C−C bonds based on low-ligand clusters, and primarily heteronuclear LLCs on supports which retain all the advantages of Klabunde systems obtained by vapour-phase synthesis.

On the other hand, the availability of $RCOX.2AlX_3$ systems, the ease in working with them, and the possibility of carrying out a wide range of selective conversions of alkanes and cycloalkanes at room temperature in their presence give grounds for regarding the discovery of superacids of this type as a fundamentally new stage in the low-temperature chemistry of paraffins.

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Metal complex catalysis of oxidation reactions: principles and problems

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ABSTRACT. The mechanisms of the oxidation of organic substrates, mainly alkenes, in the presence of mononuclear and polynuclear transition metal complexes, including cluster complexes, are examined.

The bibliography includes 121 references.

Contents

I. Introduction 1133
II. Mechanisms of the oxidation of alkenes 1133
III. Catalysis with participation of mononuclear complexes 1133
IV. Catalysis with participation of clusters 1136
V. Synthesis of catalytically active palladium clusters 1137
VI. Giant palladium clusters 1141
VII. Kinetics and mechanisms of oxidation reactions in solutions of giant palladium clusters 1145
VIII. Conclusion 1147

I. Introduction

Metal complex-catalysed liquid-phase oxidation constitutes an extensive field of chemical reactions embracing reactions occurring both in living nature and under the conditions of industrial manufacture. Industrially important reactions of this type include liquid-phase oxidation of paraffins and alkylarenes, the oxidation of alkenes to carbonyl compounds and vinyl and allyl esters, numerous alkene epoxidation processes, etc.[1]

The study of oxidation reactions has played an important role in the establishment of metal complex catalysis and in the formulation of its principles. Thus the oxidation of alkenes in the presence of palladium salts has become the first example in metal complex catalysis where it has been possible to characterise reliably all the stages and to discover the role of the catalyst components in this important multi-stage reaction. Despite the fact that the individual details remain controversial,[2] this process is probably the most thoroughly investigated also nowadays.

The authors' aim is not a laborious and exhaustive survey of oxidation reactions occurring under the influence of coordination compounds. Attention is concentrated on the reactions of unsaturated substrates. In contrast to, for example, the reactions of alkanes, in these reactions both participants in the oxidation process—the unsaturated hydrocarbon and the oxidant—are capable of interacting jointly or separately with the catalyst. This not only introduces a great variety into the mechanisms of the processes but also makes the above reaction a convenient object for the study of the principal ideas and methods of metal complex catalysis.

II. Mechanisms of the oxidation of alkenes

The functions of coordination compounds in the kinetics of oxidative homogeneous catalysis can be roughly reduced to the following schemes:

$$\begin{aligned} &M^n + Ox = A + M^m, \\ &A + Ol = P + Red; \end{aligned} \quad (1)$$

$$\begin{aligned} &M^n + Ox = M^m(A), \\ &M^m + Ol = P + M^n; \end{aligned} \quad (2)$$

$$\begin{aligned} &M^n + Ox = M^n(Ox), \\ &M^n(Ox) + Ol = P + M^n + Red; \end{aligned} \quad (3)$$

$$\begin{aligned} &M^n + Ol + Ox = Ol \cdot M^n \cdot Ox, \\ &Ol \cdot M^n \cdot Ox = P + M^n + Red; \end{aligned} \quad (4)$$

$$\begin{aligned} &M^m + Ol = M^n + P, \\ &M^n + Ox = M^m + Red, \end{aligned} \quad (5)$$

where M is the catalyst ($m > n$), Ox the oxidant, A the active form of the oxidant, Red its reduced form, Ol the substrate oxidised, and P the oxidation products.

In the first three schemes, the reaction product or its precursor arises as a consequence of the substrate being acted upon by the free (A) or bound in a complex [M^n(A)] active form of the oxidant or the complex of the catalyst and the oxidant [M^n(Ox)]. In scheme (4), the catalyst activates both the substrate and the oxidant, while in scheme (5) only the substrate is activated. Examples of olefin oxidation reactions via all the schemes indicated are known.[3,4]

III. Catalysis with participation of mononuclear complexes

A typical example of the oxidation of alkenes with participation of mononuclear transition complexes may be provided by the reaction of substituted alkenes on treatment with Fenton's reagent ($Fe^{2+}/Fe^{3+} + H_2O_2$). According to scheme (1), an iron(+3) compound acts as a reactant in the stage involving the formation of active intermediate species (free radicals). Admittedly, the aquo-complexes of iron do not merely generate free radicals [the active form of the oxidant in terms of scheme (1)] in these systems, i.e.

$$\begin{aligned} &Fe^{2+} + H_2O_2 + H^+ = Fe^{3+} + HO^\cdot + H_2O, \\ &Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2^\cdot + H^+, \end{aligned}$$

but can also influence the nature of the product formed[6] by participating in the chain propagation and termination stages.[5]

Furthermore, in the interaction of iron compounds and hydrogen peroxide there is a possibility of the appearance of species which can be regarded as iron complexes containing the coordinated radical-anion $O^{\cdot}$ or as oxygen compounds of iron(+4). It has been suggested[3,7] that the oxygenyl complexes of iron(+5) or iron(+4) are responsible for the epoxidation of alkenes in the presence of haem-containing monoxidases, for example cytochrome P-450. Porphyrin complexes of iron, chromium, and manganese, modelling this enzyme, are known.[3,4,7,8] In all these systems, the catalyst interacts with the oxidant (which may be not only an inorganic or organic peroxide but also iodosobenzene,[9] the hypochlorite ion,[10] an amine *N*-oxide,[11] or 2-sulphonyloxyaziridine[12]) and abstracts from the latter an oxygen atom, which is coordinated to the catalyst and is then transferred to the substrate. Thus the main function of the catalyst in these processes is, according to scheme (2), the formation and stabilisation of the active form of the oxidant A (the oxygen atom) and also its transfer to the substrate undergoing oxidation. Direct interaction between the substrate and the catalyst is either very weak or does not occur at all. Thus analogues of cytochrome P-450 are capable of oxidising not only alkenes but also saturated hydrocarbons whose direct interaction with catalysts of this type is unlikely. Chromium complexes of Schiff bases,[13] copper nitrate,[14] and iron(+3) chloride and acetylacetonate[15] act similarly to metalloporphyrins.

In a number of instances, when O_2 interacts with the metal complex, its activation apparently reduces to its conversion into a coordinated superoxide ion.[8,16] Thus, in the epoxidation of ethylene in the gas phase, the interaction of O_2 with a silver atom or cluster can be completed by the transfer of an *s* electron from the silver atom to a molecule of dioxygen and the formation of a coordinated superoxide ion. The attack by the "free" valence of such a complex on the ethylene molecule and the subsequent intramolecular free-radical substitution should lead to an oxide form of the silver cluster [in the simplest case to silver(+2) oxide] and epoxyethane. After the reduction of silver oxide, the active form of the catalyst is regenerated and the catalytic cycle is closed. A palladium(+2) complex of the superoxide ion was obtained recently.[17] Modelling the reaction of the silver(+1) complex with the superoxide ion, it epoxidises alkenes smoothly.

The majority of the known catalysts of epoxidation by molecular oxygen actually effect the co-oxidation of the alkene when some kind of reductant, for example, ethylene and the products of its incomplete oxidation (in the gas-phase epoxidation of ethylene on a silver catalyst), of an alkene and an alkylarene (epoxidation of propene in the chalcone process), and of an alkene and H_2 or sodium tetrahydroborate (epoxidation catalysed by porphyrin complexes of manganese).

The first system in which both oxygen atoms are used to oxidise the alkene was discovered recently.[18] It was found that the interaction of dioxygen with tetramesitylporphyrinatoruthenium(II) involves the cleavage of the O=O bond and the formation of a ruthenium(+6) complex which contains two oxo-groups. This complex attacks the alkene and converts it into an epoxide. The ruthenium(+4) complex, arising under these conditions, disproportionates, regenerating the dioxide derivative of ruthenium(+6) and a ruthenium(+2) complex which on reaction with O_2 is also converted into the porphyrin complex of dioxoruthenium(+6).

A typical example of oxidation in accordance with scheme (3) is the epoxidation of alkenes by organic peroxides in the presence of molybdenum(+6) compounds.[19] A molybdenum(+6) atom with the non-bonding d^0 configuration is incapable of forming more or less stable π-complexes with alkenes.[20] Because of this, alkenes cannot compete with rigid oxo-ligands for a site in the coordination sphere of molybdenum(+6). The kinetic data[21–23] showing that, in the oxidation of propene by ethylphenyl hydroperoxide the alkene molecule not bound in a complex is attacked by the coordinated hydroperoxide molecule, are consistent with this finding. One of the mechanisms presupposes that the molybdenum(+6) complex of the hydroperoxide acts in the same way as an organic peracid in the Prilezhaev reaction.[19,23] However, the study of the stereochemistry of the oxidation of allyl alcohols led to the conclusion[4,24,25] that an oxygen atom bound directly to the metal is transferred to the alkene. In the transition state, this atom migrates to a neighbouring O atom of the coordinated alkyl peroxide ligand. To reach final conclusions, it is essential to investigate further this industrially important reaction. However, it is significant that in all these versions of the mechanism, the role of only the activator of the oxidant is attributed to the catalyst.

The reactions in which the catalyst activates simultaneously both the oxidant and the alkene [scheme (4)] are in the first place those catalysed by rhodium[26] and palladium[27–30] compounds.

In these reactions either the alkene is inserted between the catalyst metal atom and the oxidant molecule or the oxidant, interacting with the catalyst, influences the direction of the oxidation reaction. It is possible to obtain in this way, for example, glycol ethers instead of the aldehydes and ketones formed in the absence of an oxidant.[29] In addition, there also exists routes leading to the occurrence of scheme (4), in which both the oxidant and the alkene are coordinated to the catalyst, which effects the electron transfer between them.

Evidently, for the occurrence of such mediator[31] mechanism in the case of metals with the non-bonding d^0 configuration, special requirements must be met by the alkene structure. Since the double bond in the alkene cannot be used for its coordination to a metal atom with such electronic configuration, it is essential that the alkene should contain groups directly attached to the double bond, conjugated with the latter, and capable of coordination to the metal atom. All these conditions are satisfied, for example, by pentane-2,4-dione and its analogues in the enolic form.

In solutions of molybdates or tungstates, β-dicarbonyl compounds containing at least one hydrogen atom at the central carbon atom and hence capable of enolisation are smoothly oxidised by hydrogen peroxide.[32]

A ^{1}H NMR study of this reaction[33] showed that, even after the addition of only 0.5 mol of hydrogen peroxide per mole of acetylacetone (Hacac) under conditions where the reaction products (acetic acid and CO_2) are still absent, the signal due to the CH_3 groups of the coordinated $acac^-$ vanishes, the integral intensity of the signals of both forms of free Hacac diminishes, and a broadened singlet appears at 1.96 p.p.m., whose intensity increases as H_2O_2 is added, reaching a maximum for the ratio $[H_2O_2]:[Hacac] = 2$. Analysis of these data as well as comparison of the rates of oxidation of Hacac and a hypothetical intermediate which should have arisen in the oxidation of Hacac in accordance with the Baeyer–Villiger mechanism (formaldehyde and formic acid) showed that neither the free Hacac nor the coordinated $acac^-$ undergo oxidation in accordance with the Baeyer–Villiger mechanism under the experimental conditions. A complex containing the dianion of 2,2,4,4-tetrahydroxy-3-pentanone is the observed primary oxidation product. This complex was also synthesised independently from 3,3-dihydroxypentane-2,4-dione and sodium molybdate. The study of its IR and ^{1}H NMR spectra showed that the above ligand

forms in the coordination sphere a six-membered metallocycle incorporating the central metal atom.

The oxidation of Hacac by hydrogen peroxide takes place in the coordination sphere of molybdenum(+6) .[32] The key stage of this reaction includes the transfer of electrons from the coordinated $acac^-$ to the coordinated O_2^{2-} in the inner coordination sphere of the complex. The absence of signals due to paramagnetic species in the EPR spectra at 77 and 300 K indicates the occurrence of the two-electron transfer.[33] Nevertheless, one cannot fully exclude the possibility of the occurrence of two successive one-electron processes, because the absence of the EPR signals may be associated with the exchange interaction between the paramagnetic ligands formed in the coordination sphere of the molybdenum atom. Regardless of these details of the mechanism, the resulting transfer of two electrons from the pseudo-aromatic (acac.Mo) system to the σ orbital of the O_2^{2-} fragment destabilises the latter and leads to the appearance of the O^{2-} ligand linked by multiple bonds to the central atom, which is promoted by the tendency of Mo atoms to form multiple bonds with π-donor ligands. In the coordinated $acac^+$, the positive charge is located predominantly at the C(3) atom to which the nucleophilic attack by the H_2O molecule is directed. A short-lived molybdenum complex of 3-hydroxypentane-2,4-dione is apparently formed as a result of this attack. The repeated transfer of two electrons leads to the oxidation of this intermediate, which entails also the formation of the molybdenum complex of 3,3-dihydroxypentane-2,4-dione detected in the EPR spectrum. The subsequent oxidation of the organic ligand by hydrogen peroxide apparently proceeds via the mechanism of the Baeyer–Villiger reaction with or without the participation of MoO_4^{2-}.

One cannot rule out the possibility that inner-sphere electron transfer plays a much more important role in the catalysis by metal complexes having the non-bonding d^0 configuration than has been assumed until recently. In this connection, we may note kinetic data[34,35] showing that peroxides decompose in solutions of molybdenum(+6) compounds in water and of vanadium(+5) compounds in acetic acid via the intermediate formation of complexes containing at least two peroxide molecules at the metal atom.

If the peroxide disproportionates within the coordination sphere via the transfer of two electrons in one or two rapidly succeeding elementary steps, the primary product of such decomposition should be singlet oxygen or its complex with the metal atom. Indeed, the formation of $^1O_2$ has been detected in the oxidation of aromatic compounds by peroxides in the presence of molybdenum and vanadium compounds.[36,37] In the oxidation of anthracene by hydrogen peroxide in the presence of vanadium(+5) in acetic acid solutions, the product of the addition of $^1O_2$ to the substrate is also formed.[38] In addition, anthracene fully blocks the decomposition of H_2O_2 with formation of O_2. This fact as well as comparison of the rate constants for the physical quenching of $^1O_2$ and for the reaction of $^1O_2$ with anthracene demonstrate unambiguously that anthracene is oxidised not by the free singlet oxygen but by its precursor. Kinetic data and ^{51}V NMR spectra have led to the conclusion that the active intermediate—the agent transferring $^1O_2$ to the substrate molecule—is either the peroxo-complex V(+5) $(O_2^{2-})_3$ or a complex of the type V(+5)($^1O_2$).

Another active form of oxygen, also formed via a molecular pathway on decomposition of H_2O_2 in solutions of V(+5) in acetic and trifluoroacetic acids, is ozone, whose yield is 1 and 10% respectively.[39] The oxidative hydroxylation of cyclohexane[40,41] and methane[42] and the oxidative degradation of the multiple bonds of the electron-deficient perfluorobenzene[43] and perfluoroalkenes[44,45] with formation of perfluorocarboxylic acid fluorides also occur in the same systems under mild conditions. However, it has been found[46] that the rates of oxidation of all these substrates by ozone are much lower than the rates of oxidation of the same substrates by hydrogen peroxide. Thus, despite the fact that ozone is formed in the given system, it cannot be regarded as an active intermediate in the oxidation of the substrates indicated.

The involvement in the reaction of extremely unreactive electron-deficient perfluoroalkenes, which are incapable of reacting with free singlet oxygen, as well as the low yield of epoxides show that unsaturated perfluorohydrocarbons are oxidised with participation of oxygenyl complexes of vanadium as donors of $^1O_2$.

The mechanism of the formation of the active intermediates responsible for the evolution of O_3 and the oxidation of the substrates is apparently fairly complex. This is indicated by the following facts:

1. Cyclohexane, arenes, and perfluoroarenes completely block the evolution of ozone; α-perfluoroalkenes reduce by a factor of 3–5 the yield of O_3 while β-perfluoroalkenes do not affect the yield of ozone.

2. In the joint oxidation of substrates of different nature, each preceding member of the series—cyclohexane, arene, α-perfluoroarene, and β-perfluoroalkene—completely blocks the oxidation of any subsequent member, although in their separate oxidation the rates of consumption of all these substrates are comparable.[47]

All these facts can be reasonably explained within the framework of Scheme 1 according to which several (at least four) types of active intermediates are formed in the V(+5)–H_2O_2–RCOOH system, their concentrations being stationary and each of these species being responsible for the oxidation of a substrate of only one particular type.[48]

Exactly 30 years ago, the liquid-phase alkene oxidation reactions catalysed by palladium(+2) compounds were discovered:[49–51]

$$\begin{aligned} &C_2H_4 + {}^1/_2 O_2 = CH_3CHO, \\ &C_2H_4 + {}^1/_2 O_2 + AcOH = CH_2{=}CHOAc + H_2O, \\ &C_2H_4 + {}^1/_2 O_2 + 2ROH = CH_3CH(OR)_2 + H_2O. \end{aligned} \quad (6)$$

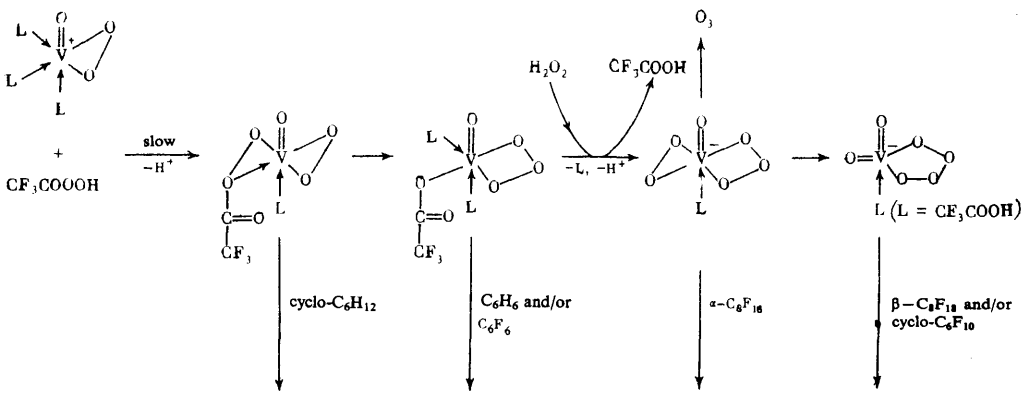
An important feature of these reactions, proceeding in accordance with scheme (5), is that the substrate activation (the key stage in which the alkene molecule is converted into a precursor of the final product) proceeds in the inner coordination sphere of the mononuclear palladium(+2) complex:[20]

$$\begin{aligned} &PdCl_4^{2-} + C_2H_4 = PdCl_3(\pi\text{-}C_2H_4)^- + Cl^-, \\ &PdCl_3(\pi\text{-}C_2H_4)^- + H_2O = PdCl_2(H_2O)(\pi\text{-}C_2H_4) + Cl^-, \\ &PdCl_2(H_2O)(\pi\text{-}C_2H_4) = PdCl_2(OH)(\pi\text{-}C_2H_4)^- + H^+, \\ &PdCl_2(OH)(\pi\text{-}C_2H_4)^- \rightarrow \sigma\text{-}Cl_2Pd{-}CH_2CH_2OH^-, \\ &\sigma\text{-}Cl_2Pd{-}CH_2CH_2OH^- \rightarrow Pd^0 + 2Cl^- + CH_3CHO, \\ &Pd^0 + Ox + 4Cl^- \rightarrow PdCl_4^{2-} + Red. \end{aligned} \quad (7)$$

At high palladium(+2) concentrations, dinuclear palladium(+2) complexes of the type $Pd_2Cl_6^{2-}$ also participate in these reactions, but the mechanism of their action differs fundamentally from that presented in scheme (7) for mononuclear complexes.[52]

Since the discovery by Shilov and Shteinman[53,54] of deuterium exchange between methane and D_2O in the presence of platinum salts, a vigorous search is being prosecuted throughout the world for transition metal complexes capable of catalysing reactions involving the oxidative functionalisation of alkanes. The recently published

Scheme 1



oxidation products

communications[55,56] about the oxidation of methane and certain other hydrocarbons by palladium(+2) salts may be included among the number of recent attempts to achieve the oxidation of an alkane in accordance with scheme (5). Palladium(+2) is usually introduced in the form of the trimeric acetate $Pd_3(OAc)_6$ into the trifluoroacetic acid solution where it is in all probability converted into the monomeric $Pd(OCOCF_3)_2$. Under fairly mild conditions, at 80 °C and 60–70 atm, methyl trifluoroacetate was obtained from methane in 60% yield:

$$CH_4 + Pd(OCOCF_3)_2 = CH_3OCOCF_3 + Pd^0 + CF_3COOH. \quad (8)$$

If this reaction is combined with the reoxidation of zerovalent palladium to palladium(+2), as had been done earlier in the oxidation of alkenes via reaction (6), it might be possible, in principle, to achieve the liquid-phase catalytic oxidation of methane by oxygen. Unfortunately, so far it has not been possible to reproduce in our laboratories the results obtained in the above studies.[55,56]

In the search for complexes of other transition metals capable of reacting with methane, it has recently been observed[57,58] that cobalt(+3) trifluoroacetate is reduced by methane under comparatively mild conditions (CF_3COOH solution, 150–180 °C, 10–40 atm), converting it into methyl trifluoroacetate in a nearly quantitative yield [90 ± 10% with respect to Co(+3)]:

$$CH_4 + 2Co(OCOCF_3)_3 = CH_3OCOCF_3 + 2Co(OCOCF_3)_2 + CF_3COOH. \quad (9)$$

In the presence of oxygen, the cobalt(+2) formed is oxidised to cobalt(+3):

$$Co(OCOCF_3)_2 + {}^1/_2 O_2 + CF_3COOH = Co(OCOCF_3)_3 + H_2O,$$

which made it possible to achieve for the first time the highly selective catalytic conversion of methane into methyl trifluoroacetate:[58]

$$CH_4 + {}^1/_2 O_2 + CF_3COOH = CH_3OCOCF_3 + H_2O. \quad (10)$$

The state of cobalt(+3) and cobalt(+2) in these solutions has not so far been investigated. There is no complete certainty that the cobalt(+3) complex is in fact the electrophile which attacks the methane molecule. One cannot rule out the possibility that reaction (10) proceeds as a result of the participation of the oxygenyl complexes of cobalt(+4), which may have a polynuclear structure.

IV. Catalysis with participation of clusters

A considerable amount of data indicating the existence of a specific field of catalysis in which the substrate is activated by polynuclear, mainly cluster, compounds of transition metals has accumulated recently. Among such palladium cluster-catalysed reactions, one may include, for example:

positional and geometrical isomerisation of alkenes;[59]
dimerisation and oligomerisation of alkenes;[60]
hydrogenation of acetylenes, dienes, nitro-compounds, quinones, and other unsaturated compounds;[61,62]
oxidative dehydrogenation of cyclohexene;[59]
oxidative acetoxylation of alkenes[63] and alkylarenes;[64]
alkoxycarbonylation of acetylene.[65]

The oxidative substitution of a hydrogen atom in alkenes (ethylene, propene) by the acetoxy-group, which has been achieved industrially, occupies a special place among these reactions:

$$C_nH_{2n} + {}^1/_2 O_2 + AcOH \xrightarrow[180\,^\circ C]{Pd/SiO_2} C_nH_{2n-1}OAc + H_2O. \quad (11)$$

This process is carried out in the vapour phase using metallic palladium with added alkali metal acetates on the surface of a porous carrier as the catalyst.[66]

It was initially postulated that the heterogeneous version of reaction (11) also proceeds via the mechanism characteristic of reactions (6) mentioned above, with participation of the mononuclear palladium(+2) complexes, via alternating stages in which palladium(+2) is reduced and zerovalent palladium is oxidised:

$$Pd(+2) + C_nH_{2n} + AcOH \rightarrow Pd(0) + C_nH_{2n-1}OAc + H_2O,$$
$$Pd(0) + {}^1/_2 O_2 \rightarrow Pd(+2) + H_2O.$$

However, the hypothesis of the involvement of palladium(+2) in reaction (11) agrees poorly with data concerning the selectivity of the oxidative acetoxylation of propene and ethylene.[67] Thus, in the

oxidation of propene by palladium(+2) acetate in solution in acetic acid, the yield of allyl acetate, which is high in the absence of water and at low temperatures (94% at 25 °C), falls sharply on raising the temperature and on increasing the water content (4% at 118 °C; the remainder consists of acetone and other side products).[68] On the other hand, in the presence of a heterogeneous palladium catalyst, the selectivity with respect to allyl acetate remains constantly high (~90%) even on raising the temperature to 180 °C and the water content to 10%.[69]

On interaction of $Pd(OAc)_2$ with the $C_3H_6-O_2$ mixture in solution in acetic acid containing NaOAc, propene is oxidised without the consumption of oxygen solely as a result of the reduction of palladium(+2). Under these conditions, a mixture of products is formed (isopropenyl acetate, n-propenyl acetate, allyl acetate, and acetone) with the same quantitative composition as in the absence of O_2.[70] However, after the complete reduction of palladium(+2), a slower catalytic reaction begins in which O_2 is consumed and the product of the allylic oxidation of propene (allyl acetate) is formed in a high yield.[67]

Significant differences between the selectivities of the action of palladium(+2) and heterogeneous palladium catalysts have been observed also in the oxidation of alkylarenes in the presence of carboxylic acids.[71,72] On treatment with palladium(+2) in solution in acetic or trifluoroacetic acid, toluene undergoes mainly oxidative coupling via the benzene rings with formation of a mixture of isomeric (*o*-, *m*-, and *p*-) bitolyls:

$$2C_6H_5CH_3 + Pd(+2) = CH_3C_6H_4-C_6H_4CH_3 + Pd(0) + 2H^+.$$

The reoxidation of the reduced form of palladium with oxygen makes it possible to carry out the process under catalytic conditions (with respect to palladium):

$$2C_6H_5CH_3 + {}^1/_2\,O_2 = CH_3C_6H_4-C_6H_4CH_3 + H_2O.$$

So long as an appreciable amount of reduced palladium does not accumulate in the system, the above toluene oxidation pathway remains unchanged. However, the accumulation of metallic palladium or the introduction of freshly prepared palladium black leads to a sharp alteration of the composition of the products. The main reaction pathway becomes the benzyl oxidation—the oxidative acetoxylation of toluene in the side chain: $C_6H_5CH_3 + \frac{1}{2}O_2 + AcOH = C_6H_5CH_2OAc = H_2O$.

Finally, the thermal instability of palladium(+2) carboxylates at temperatures above 100 °C, where the oxidative acetoxylation of alkenes and alkylarenes in the presence of a heterogeneous catalyst proceeds most readily at 150–200 °C, constitutes evidence against the participation of palladium(+2) in the heterogeneous-catalytic oxidation of alkenes.[63] All these data suggest that the active centres of the heterogeneous palladium catalysts, responsible for the oxidative acetoxylation of alkenes and alkylarenes, contain not palladium(+2) but palladium in a lower oxidation state.

As for other platinum metals, the lower oxidation state of palladium is represented, with few exceptions, by cluster compounds. However, stable coordinatively unsaturated clusters are as a rule catalytically inactive. Under the conditions of the catalytic reaction, it is also not possible to rule out the possibility of the decomposition of the cluster complex with formation of the catalytically active metal phase. Therefore, in order to elucidate the principal features of cluster catalysis, it is essential not only to synthesise a cluster suitable for the occurrence of the catalytic reaction but also it is necessary to make sure that the cluster and not its decomposition product is responsible for the catalysis of the given reaction.

V. Synthesis of catalytically active palladium clusters

One of the most effective methods of synthesis of transition metal clusters is based on the monocarbonyls and polycarbonyls of these metals.[73] Unfortunately, palladium does not form binary carbonyls stable under the usual conditions.[74] Palladium complexes containing other ligands in addition to CO are therefore used as the initial compounds.

When solutions of palladium(+2) salts are treated with CO, palladium(+2) is usually reduced to the metal. Thus the reduction of $Pd(OAc)_2$ by carbon monoxide in glacial acetic acid containing alkali metal acetates leads to the formation of metallic palladium, acetic anhydride, and CO_2:[21]

$$Pd(OAc)_2 + CO \rightarrow Pd^0 + Ac_2O + CO_2.$$

In carboxylic acids or carboxylic acid + benzene mixtures in the absence of alkali metal acetates, fairly stable complexes [(RCOO).Pd(CO)].*n*RCOOH, where n = 0.5 or 0, were obtained. Thus carbonylation of palladium(+2) acetate in glacial acetic acid at 50 °C leads to the compound $Pd_4(CO)_4(OAc)_4.2AcOH$. According to X-ray diffraction data,[76] the main structural unit of these crystals consists of the tetranuclear clusters $Pd_4(CO)_4(OAc)_4$ (PCA) with a rectangular metallic core (Fig. 1). The sides of the rectangle spanned by acetate bridges are longer (2.909 Å), while those linked by carbonyl bridges are shorter (2.603 Å) than the Pd–Pd distance in metallic palladium (2.751 Å).

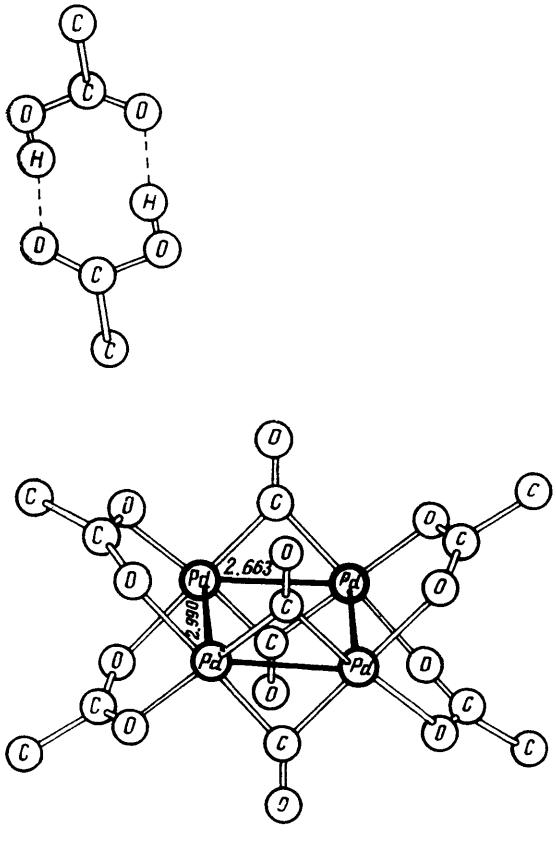


Figure 1. The structure of the cluster $Pd_4(CO)_4(OAc)_4.2AcOH$.

The reactions of $Pd(OCOEt)_2$ and $Pd(OCOPh)_2$ with CO afford the analogous clusters $Pd_4(CO)_4(OCOEt)_4$ and $Pd_4(CO)_4(OCOPh)_4$.[77] The similarity of the chemical properties and spectroscopic characteristics of these compounds suggested that they are all constructed similarly to PCA. Thus the synthesis of PCA, described by the equation

$$4Pd(OAc)_2+8CO=Pd_4(CO)_4(OAc)_4+2Ac_2O+4CO_2, \quad (12)$$

represents a general route to palladium(+1) carbonyl carboxylates.[77]

Studies on the kinetics and intermediates of reaction (12) led to the conclusion[78] that the formation of PCA from the trimeric palladium(+2) acetate is a reaction of the type of reductive condensation and involves the following stages:

(1) insertion of CO in the Pd–OAc bond;

(2) elimination of CO_2 with formation of the acyl fragment $Pd-C(O)-CH_3$;

(3) liberation of a molecule of acetic anhydride Ac_2O and the formation of the Pd–Pd bond.

The coordinated acetate groups in PCA are readily substituted by other carboxylates on interaction of the corresponding acids with PCA:

$$Pd_4(CO)_4(OAc)_4 \xrightarrow[-AcOH]{RCOOH} [Pd(CO)(OCOR)]_4, \quad R = CD_3,\ Et,\ Ph,\ CF_3,\ CCl_3,\ CH_2Cl. \quad (13)$$

The similarity of the IR spectra, chemical behaviour, and stoichiometry of these compounds with the data for PCA suggests that all these complexes are analogues of PCA.[77]

Treatment of PCA with inorganic acids, for example, hydrochloric acid, also leads to the substitution of the acetate groups by Cl^-, but the carbonyl chloride complexes formed are unstable. It might have been supposed that the substitution of the acetate groups in PCA by an involved metal complex anion, for example, carbonyl metallate, does not lead to the decomposition of the metallic core and would make it possible to obtain a heteronuclear palladium-containing cluster.

Indeed, the interaction of PCA with $Na[CpMo(CO)_3]$ yielded the anionic octanuclear cluster $Na_2\{Pd[Mo(CO)_3Cp]\}_4.2THF$.[79] According to X-ray diffraction data, the principal structural units of crystals of this compound are the centrosymmetric anion $\{Pd[Mo(CO)_3Cp]\}_4^{2-}$, two Na^+ cations, and two THF molecules. The Pd atoms are arranged at the vertices of the square (Pd–Pd = 2.675–2.691 Å) (Fig. 2). Each Mo atom forms an almost regular triangle with two Pd atoms (Pd–Mo = 2.723–2.741 Å) and all the metal atoms lie in the same plane.

The formation of the octanuclear cluster involves not only the substitution of the acetate ligands by the anions $CpMo(CO)_3^-$ but also the displacement of the neutral CO molecules. The liberated vacancies in the coordination sphere of palladium are occupied by the CO molecules coordinated to Mo, which are converted into bridges linking atoms of different metals. Apparently the process is not restricted to the substitution of ligands: during the reaction, Pd(+1) atoms are reduced, probably as a result of the one-electron oxidation of the $CpMo(CO)_3^-$ anions. If it is assumed that the Mo atoms forming part of this complex have a zero oxidation state, which obtains in the initial compound, then the observed reaction can be regarded as the reduction of Pd(+1) to Pd(+5):

$$Pd_4(CO)_4(OAc)_4+6Na[CpMo(CO)_3]=Na_2[Pd_4Mo_4Cp_4(CO)_{12}]+4CO+[CpMo(CO)_3]_2+4NaOAc. \quad (14)$$

Reactions (13) and (14) are examples of the substitution of the acido-ligands in PCA by other acido-groups. The substitution of the neutral carbonyl ligand is observed on interaction of PCA with diphenyldiazomethane.[80] The interaction of PCA with Ph_2CN_2 in benzene leads to the displacement of the CO groups and the formation of a complex containing diphenylcarbene as the ligand:

$$Pd_4(CO)_4(OAc)_4+Ph_2CN_2\rightarrow Pd_4(CPh_2)_4(OAc)_4+CO+4N_2.$$

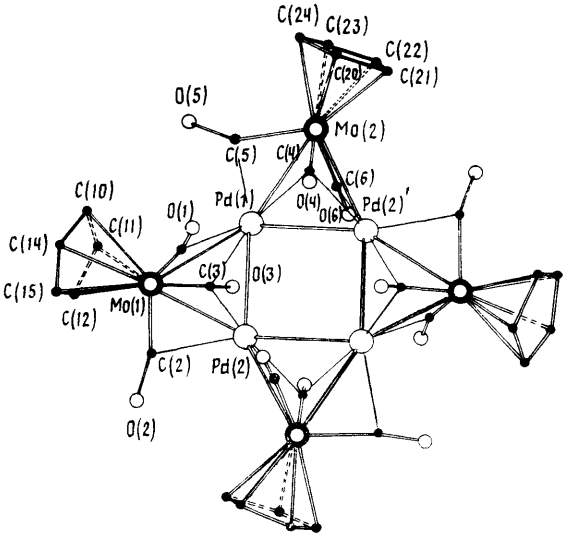


Figure 2. The structure of the cluster dianion $\{Pd_4[CpMo(CO)_3]_4\}^{2-}$.

The composition of the resulting complex as well as the results of physicochemical studies (elemental analysis, IR and ^1H NMR spectra, molecular weight measurements) can be equally attributed both to the formation of a complex with carbene ligands and a π-complex with tetraphenylethylene. However, the presence of carbene ligands in the complex is indicated by reactions leading to products characteristic of the free carbenes. Thus hydrogenation of the complex in benzene at 20 °C and 1 atm H_2 pressure leads to the dissociation of the Pd–C bonds and the formation of diphenylmethane:[81]

$$...Pd=CPh_2+H_2\rightarrow ...Pd+Ph_2CH_2.$$

Alkaline hydrolysis of the complex affords diphenylmethanol together with diphenylmethane and benzophenone:

$$...Pd=CPh_2+H_2O \xrightarrow{EtOH,\ KOH} ...Pd+Ph_2CHOH.$$

Interaction with alkenes results in the formation of the products of the cycloaddition of the carbene to the alkene, which is characteristic of both the free carbenes and of their complexes. For example, the reaction of the complex with hex-1-ene leads to 2-butyl-1,1-diphenyl-cyclopropane:

$$...Pd=CPh_2+CH_3(CH_2)_3CH=CH_2 \rightarrow ...Pd+CH_3(CH_2)_3CH(CPh_2)CH_2.$$

The structure of the carbene complex was investigated by the EXAFS method.[82] The results confirmed the hypothesis that a rectangular metallic core is present (Fig. 3).

PCA reacts in a very complex manner with ligands such as PPh_3, pyridine (Py), phenanthroline (Phen), diphosphine (Diphos), and bipyridyl (Bipy). Depending on the initial Pd:ligand concentration ratio, complexes of different composition are formed.[83] The palladium compounds produced for the ratio $[Pd]_\Sigma:[L]_\Sigma \geqslant 2$ (L = ligand) are fairly unstable. As $[Pd]_\Sigma:[L]_\Sigma$ diminishes, more stable complexes are formed.

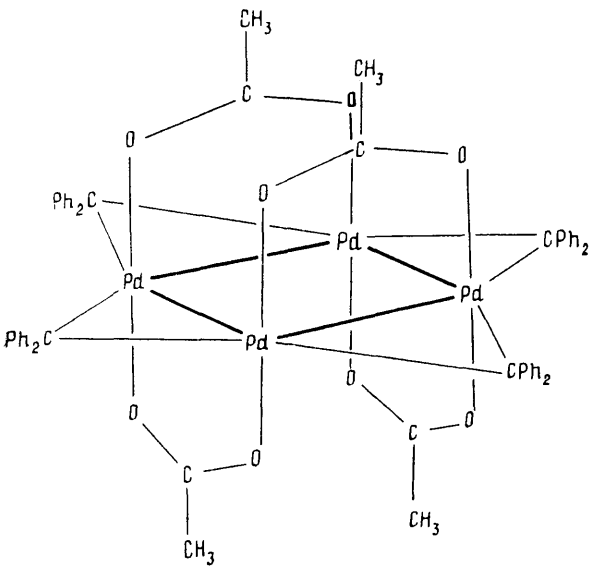


Figure 3. The structure of the carbene cluster $Pd_4(CPh_2)_4(OAc)_4$ according to EXAFS data.

The interaction of PCA with pyridine and its alkyl derivatives, using the ratio $[Pd]_\Sigma:[L]_\Sigma = 1:1$, involves the disproportionation of the Pd(+1) to Pd(+2) and Pd(0):

$$Pd_4(CO)_4(OAc)_4+4Py=2Pd^0+2PdPy_2(OAc)_2+4CO.$$

The reaction of PCA with diphosphine in benzene makes it possible to obtain the complex $Pd_2(Diphos)_2(CO)(OAc)_2.C_6H_6$:[84]

$$Pd_4(CO)_4(OAc)_4+4Diphos=2Pd_2(Diphos)_2(CO)(OAc)_2+2CO.$$

The interaction of PCA with a (5–10)-fold excess of diphosphine in tetrahydrofuran (THF) leads to the cationic complex $[Pd_2(\mu\text{-}CO)(Diphos)_4]^{2+}(OAc)_2$ with a different coordination of the diphosphine ligands:

$$Pd_4(CO)_4(OAc)_4+8Diphos=2Pd_2(CO)(Diphos)_4(OAc)_2+2CO.$$

When PCA is treated with PPh_3, the complex $Pd_2(CO).(PPh_3)_2(OAc)_2$ is formed:

$$Pd_4(CO)_4(OAc)_4+4PPh_3=2Pd_2(CO)(PPh_3)_2(OAc)_2+2CO.$$

This complex contains a CO bridging group [ν(CO) = 1800 cm^{-1}]. Depending on the conditions of the synthesis, compounds differing in the mode of coordination of the acetate groups are produced. Thus, when the reaction was carried out in solution in THF, a complex with acetate bridges was obtained [ν_s(COO) = 1530 cm^{-1}, ν_{as}(COO) = 1400 cm^{-1}, and $\Delta\nu$ = 130 cm^{-1}], while the reaction of PCA with PPh_3 in benzene leads to a compound with terminal OAc groups [ν_s(COO) = 1610 cm^{-1}, ν_{as}(COO) = 1350 cm^{-1}, $\Delta\nu$ = 260 cm^{-1}]. The complex is unstable in solution and gradually disproportionates to Pd(+2) and Pd(0). The latter was isolated in the form of the mononuclear complex $Pd(PPh_3)_3$.[84]

In the case of bipyridyl at an initial concentration of 0.5 M and a PCA concentration of 5×10^{-3} M, all the coordinated CO molecules are displaced:[83]

$$Pd_4(CO)_4(OAc)_4+2Bipy=2Pd_2(Bipy)(OAc)_2+4CO.$$

At low bipyridyl concentrations ($\leqslant 5 \times 10^{-3}$ M), only half of the coordinated CO molecules are displaced from PCA:

$$Pd_4(CO)_4(OAc)_4+2Bipy=2Pd_2(Bipy)(CO)(OAc)_2+2CO.$$

In contrast to bipyridyl, *o*-phenanthroline at 20 °C displaces from PCA only half of the coordinated CO molecules at the highest ligand concentrations:

$$Pd_4(CO)_4(OAc)_4+4Phen=2Pd_2(CO)(Phen)_2(OAc)_2+2CO.$$

The last two complexes were also obtained directly by reducing with carbon monoxide a solution in acetic acid containing $Pd(OAc)_2$ and L.[84]

The interaction of PCA with *o*-phenanthroline in the proportions $[Pd]_\Sigma:[Phen]_\Sigma = 1:1$ in solution in acetic acid affords the complex $Pd_4(CO)_2(Phen)_4(OAc)_4$:[85]

$$Pd_4(CO)_4(OAc)_4+4Phen=Pd_4(CO)_2(Phen)_4(OAc)_4+2CO.$$

The same complex was obtained by reducing with carbon monoxide palladium(+2) acetate in solution in acetic acid containing *o*-phenanthroline. According to X-ray diffraction data, the crystals of the complex contain as the main structural unit the tetrahedral cluster cation $[Pd_4(CO)_2(Phen)_4]^{4+}$ (Fig. 4). The OAc^- ligands are not linked directly to the palladium atoms but are located in the outer sphere. On formation of this complex from PCA, all the metal–metal distances change significantly: the lengths of the Pd–Pd bonds in the Pd(μ-CO)Pd fragments increase to 2.890 Å (in PCA this distance is 2.663 Å). None of the acetate groups in $[Pd_4(CO)_2(Phen)_4]^{4+}$ are coordinated to the palladium atoms, as in PCA, but are located in the outer sphere as the OAc^- anions.

The complexes obtained behave as moderately strong electrolytes in aqueous solution. They undergo a reversible substitution of OAc^- by X^- anions:

$$Pd_2(CO)Phen_2(OAc)_2 \underset{OAc}{\overset{X^-}{\rightleftarrows}} Pd_2(CO)Phen_2X_2,$$

$$X^- = ClO_4^-,\ Cl^-,\ HSO_4^-,\ Cl_3CCOO^-,\ F_3CCOO^-,\ CNS^-.$$

Such complexes have been isolated and characterised by elemental analysis and IR spectroscopy.[83]

The study of PCA and its derivatives showed that none of these complexes react with ethylene, propene, and toluene in carboxylic acids and do not exhibit a catalytic activity in the oxidation of these

hydrocarbons by molecular O_2. A low catalytic activity in the oxidation of propene to allyl acetate and of toluene to benzyl acetate [~0.1 mol (mol Pd)$^{-1}$ h^{-1} at 90 °C and 1 atm O_2] was observed only in the case of PCA after the latter had been kept in acetic acid solution containing 1 M sodium acetate for 0.5–1 h at 60–90 °C under a O_2 atmosphere. During this operation, PCA decomposes with formation of palladium black: $Pd_4(CO)_4(OAc)_4 = 4\,Pd + 2CO + 2CO_2 + 2Ac_2O$, while the CO, evolved as a result of this reaction and sorbed on the surface of metallic palladium, is oxidised by oxygen to CO_2, which makes the surface of the metal accessible to hydrocarbons.

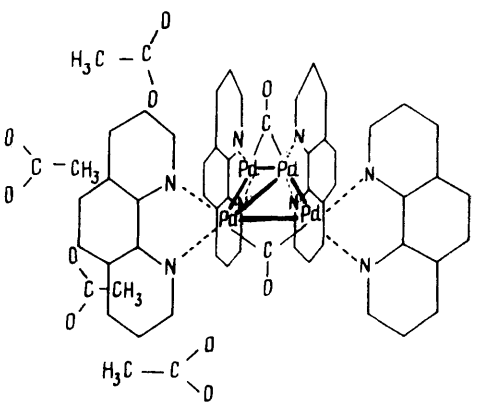
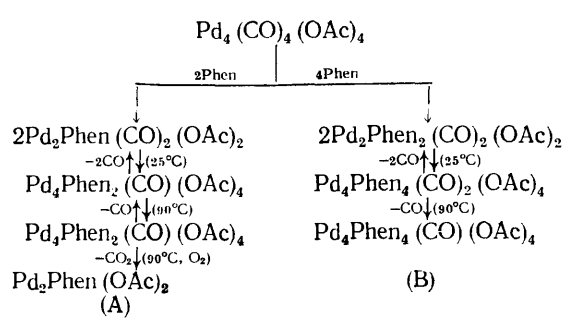


Figure 4. The structure of the cluster $[Pd_4(CO)_2Phen_4](OAc)_4$.

None of the remaining carbonyl carboxylate clusters described in this section exhibits a catalytic activity either because of their coordinative unsaturation and a low tendency towards the formation of intermediate complexes with an alkene or alkylarene molecule or as a consequence of their decomposition to other relatively inactive and also coordinatively unsaturated palladium complexes.

In contrast to this, the more labile palladium complexes formed in the reaction of PCA with *o*-phenanthroline or bipyridyl in solution in acetic acid using a concentration ratio $[Pd]_\Sigma:[L]_\Sigma \geqslant 1:1$ proved to be catalytically active.[64]

Studies on the reactions occurring between PCA and *o*-phenanthroline at different concentrations in solution in acetic acid led to the conclusion that the reactions in this system can be represented by the following scheme.[64]



The complexes of the (B) series, formed at comparatively high *o*-phenanthroline concentrations, lead at 25 °C to the stable cationic cluster $Pd_4Phen_4(CO)_2(OAc)_4$ with a tetrahedral metallic core (see above). The more labile series (A) complexes, formed at a concentration [Phen] $\leqslant 10^{-2}$ M are catalytically inactive so long as their composition includes even one coordinated CO molecule. The removal of the latter is achieved only in an O_2 atmosphere at $T \geqslant 90$ °C, which leads to the formation of a catalytically active substance whose elemental composition corresponds approximately to the formula $Pd_2(Phen)(OAc)_2$.[64]

A more exact chemical composition of the palladium-containing complex responsible for the catalytic activity in this system was not determined. Nevertheless the study of its catalytic properties permitted the conclusion that the catalytic reactions proceed in this instance without the involvement of divalent palladium. This is indicated by the following data:[67]

1. The reduction of palladium(+2) in acetic acid containing alkenes and toluene is sharply inhibited after the introduction of 0.1–0.5 M mol of *o*-phenanthroline, bipyridyl, or PPh_3 per mole of palladium. The addition of these ligands to a system based on PCA + Phen which has passed the catalyst formation stage [in accordance with scheme (A)] hardly affects the rate of the oxidative acetoxylation of propene and toluene even at an added ligand concentration exceeding by a factor of 2–5 the overall palladium concentration.

2. In the oxidation of propene in the catalytic system indicated, allyl acetate is formed in 100 ± 5% yield relative to the propene which has reacted and even traces of acetone, propenyl acetate, or isopropenyl acetate are absent; in the oxidation of toluene, there are no oxidative coupling and ring-acetoxylation products, only the products of the oxidative acetoxylation of the side chain being formed—benzyl acetate (⩾90%) and benzylidene diacetate (⩽10%).

3. The addition of 10–15% of water to a solution of the catalyst based on PCA + Phen does not lead to the appearance of acetaldehyde on oxidation of ethylene and acetone accompanying the oxidation of propene, which is not characteristic of catalytic systems based on palladium(+2).

4. When $Pd(OAc)_2$ is added to the catalytic system indicated, the selectivity of the oxidation of ethylene and toluene falls as a consequence of the formation of vinyl ethers and bitolyl respectively; acetone appears in the propene oxidation products.

Catalytic systems based on PCA + Phen (or Bipy, PPh_3) exhibit a comparatively high activity in the oxidative acetoxylation of ethylene, propene, and toluene under mild conditions (60–100 °C, 1 atm, 5–10 mol of the ester per mole of palladium per hour), which exceeds the activity of palladium black by a factor of 2–10. A deficiency of these catalytic systems is their low stability as a function of time: after continuous operation for 3–10 h at 60–90 °C, a deposit of palladium black is produced and the activity falls by a factor of 3–5.[64]

Apart from the oxidative acetoxylation reactions, the system based on PCA + Phen makes it possible to achieve the catalytic oxidative acetoxylation reaction. Thus, in solution in methanol propene is oxidised to allyl methyl ether:[86]

$$CH_2{=}CHMe + MeOH + {}^1/_2O_2 = CH_2{=}CHCH_2OMe + H_2O,$$

whereas isobutene is oxidised to methallyl methyl ether:

$$CH_2{=}CMe_2 + MeOH + {}^1/_2O_2 = CH_2{=}CMeCH_2OMe + H_2O.$$

Since catalytic activity is shown by products of the reaction of palladium(+1) carbonyl acetate not containing coordinated CO, it is useful to obtain a catalytically active palladium cluster by another procedure, bypassing the carbonyl complex formation stage.

It was observed[88] that solutions catalytically active in oxidative alkene acetoxylation reactions are formed when $Pd(OAc)_2$ is reduced in acetic acid containing *o*-phenanthroline, bipyridyl, and their analogues by various reductants, among which H_2 is the most convenient. The dependence of the catalytic activity on the overall content of the ligand L passes through a maximum in the region of ratios $[Pd]_\Sigma:[L]_\Sigma$ from 2:1 to 4:1.[63,88]

If it is postulated that the ratio $\{[Pd]_\Sigma:[L]_\Sigma\}_{max}$ indicates the composition of the compound responsible for the catalysis, one may conclude that the oxidation of alkenes is catalysed by ligand-deficient cluster compounds. In order to elucidate the nature of these compounds, their compositions and structures as well as the stoichiometry of the stages leading to the formation of catalytically active compounds were investigated.

The product of the reduction of palladium(+2) acetate by hydrogen in solution in acetic acid containing 0.5 mol of *o*-phenanthroline per palladium atom was isolated. It is an X-ray-amorphous substance whose composition corresponds to the very simple formula $Pd_4(Phen)(OAc)_2$.[89] It has been shown by volumetric measurements that 1.3 ± 0.05 mol of H_2 is consumed per mole of palladium(+2) in the formation of this substance, which could correspond to the following reaction stoichiometry:

$$4Pd_3(OAc)_6+3Phen+15H_2=3Pd_4Phen(OAc)_2H_4+6AcOH.$$

In order to confirm the conclusion that the complex is of the hydride type, its ^1H NMR spectra were investigated. In the range of chemical shifts δ = 0 to −80 p.p.m., no signals due to hydride atoms were detected in the high-resolution spectra (25 kHz frequency range) of solutions of the complex in CD_3OD, although a broad band with a maximum in the range δ = −30 to −50 p.p.m. (width 5 kHz) was found in the broad-band spectrum (250 kHz frequency range). Similar data have been obtained for the analogue of this complex containing bipyridyl instead of *o*-phenanthroline. The spectrum of the solid specimen, recorded with rotation at the "magic angle", contains three somewhat narrower (~2 kHz) bands in the range of δ from −35 to −50 p.p.m. These data confirm the hypothesis that the complexes obtained are of the hydride type.

The appreciable broadening of the hydride signal can be explained by the fact that the Pd atoms in these complexes form a polynuclear structure with a system of metal−metal bonds similar to that in the lattice of metallic palladium or its hydride phases. The protons of the $OCOCH_3$ groups are observed in the ^1H NMR spectrum as a narrow signal at δ = 2.0 p.p.m., while the signal of the *o*-phenanthroline protons consists of a complex unresolved multiplet in the range of δ from 6 to 9 p.p.m. The broadening of the usually resolved multiplet of the *o*-phenanthroline protons can be explained by the coordination of this ligand to the palladium atoms of the paramagnetic metallopolymer. This was confirmed by the weak temperature-independent paramagnetism found for the complex ($\chi_g^{300} = 0.5 \times 10^{-6}$ CGSU).[90]

The study of this complex by high-resolution transmission electron microscopy showed that its particles contain an approximately spherical metallic core 20 ± 5 Å in diameter.[89] The observed value agrees well with the average diameter of the particles obtained by the small angle X-ray scattering method (18 ± 5 Å).

The study of solid specimens of the hydrido-complex by the EXAFS method yielded the radial distribution curve for the atoms (RDA) on which there is one maximum corresponding to the Pd−N = 2.1 ± 0.1 Å interatomic distance and a signle peak corresponding to the Pd−Pd = 2.62 ± 0.05 Å distance. Maxima corresponding to more remote palladium atoms were not detected, which may be explained by the absence of long-range order in their arrangements as a consequence of the not completely regular incorporation of the H atoms in the core of the complex.[89]

The observed dimensions of the metallic core of the hydrido-complex molecule make it possible to estimate the value of *n* in the idealised formula $[Pd_4Phen(OAc)_2H_4]_n$ as approximately 100 on the assumption that the packing density of the palladium atoms in the core of this cluster is the same as in the metallic palladium lattice.

The chemical properties of the hydrido-complex indicate its high reactivity. Table 1 shows that treatment of the polynuclear hydrido-complex with various reagents leads as a rule to unstable products which decompose into mononuclear or oligonuclear palladium complexes. In contrast to this, the reaction with O_2 leads to the formation of clusters in which a massive metallic core is retained. These clusters proved to be effective catalysts of many oxidation reactions.

Table 1. The principal palladium-containing products of the reaction of a polynuclear hydrido-complex with various reagents at 293 K.

Reagent	Solvent, reaction time	Reaction products
Hg	AcOH, 2 h	H_2, Pd amalgam
PPh_3	DMF, 3 h	H_2, $Pd(PPh_3)_3$
CO	RCOOH (R=Me, Et, t-Bu), 1−3 h	$[Pd_4Phen_3(CO)_3H_2(OCOR)_3]_n$*
NO	AcOH, 1 h	$Pd_4(NO)_2(OAc)_6$
$H_2NCON(Me)NO$	DMF, 24 h	PdPhen$(NCO)_2$ (Ref.92)
Tetrachloro-*o*-benzoquinone	DMF, 3 h	$(C_6O_2Cl_4)Pd(DmPhen)$**
$PhenH^+X$, where X=BPh_4, PF_6, AsF_6	AcOH, 1−3 h	$PdPhen_2X$
O_2	AcOH, 10−30 min	$[Pd_9Phen(OAc)_3]_{60}$

*Polynuclear hydride complex with $n \simeq 2.3$.[93]

**DmPhen = 2,9-dimethyl-1,10-phenthroline was used instead of Phen in the synthesis of the hydrido-complex.

VI. Giant palladium clusters

In the reaction with O_2 the polynuclear hydrido-complex loses the hydride atoms forming part of its composition, which are bound in H_2O. A small proportion of the palladium atoms are then oxidised to palladium(+2) complexes, while the main bulk of them are converted into a cluster type substance whose simplest formula is $Pd_9(Phen)(OAc)_3$ (I) and which is stable in air and is soluble, like the hydrido-complex, in water and polar organic solvents.[94]

1. The structure of giant palladium clusters

The rate of sedimentation of compound (I) in aqueous solution obtained with the aid of an ultracentrifuge made it possible to estimate the molecular weight as (1.0 ± 0.05) × 10^5. More definite

information about the size of the molecules of compound (I) was obtained with the aid of the small angle X-ray diffraction method, high-resolution transmission electron microscopy, and electron diffraction.[90,91,94,95]

On the electron photomicrographs, the metallic cores of the molecules of compound (I) appear as almost regular spherical particles 26 ± 3.5 Å in diameter. The electron diffraction patterns, recorded for the same specimens of compound (I), contain 5–6 diffuse rings whose positions are close to those for metallic palladium.

The similarity between the sets of interplanar spacings for compound (I) and metallic palladium might indicate the identity of the principal parameters of the structures of the metallic core of compound (I) and the space-centred cubic lattice of metallic palladium. However, this hypothesis conflicts with EXAFS data, which definitely indicate eicosahedral packing of the palladium atoms in the molecules of compound (I) (see below). It is reasonable to postulate that the cause of the similarity between the electron diffraction patterns of compound (I) and metallic palladium is the degradation of the molecules of compound (I) leading to the formation of metallic particles on exposure to the electron beam.

The destructive effect of the electron beam on the cluster molecules was observed in electron microscope studies on the $Au_{55}(PPh_3)_{12}Cl_6$ [96,97] and $[Ni_{38}Pt_6(CO)_{48}H](Me_3NCH_2Ph)_5$ [98] clusters. As a result of the loss of ligands, the initial eicosahedral skeleton of the cluster can relax to a crystallite with a cubic face-centred lattice (for example in the form of a cubo-octahedron). It may be that similar processes occurred also in the electron microscope study of the recently synthesised platinum cluster $Pt_{309}L_{36}O_{30\pm10}$ (L = bis-sulphophenyl-1,10-phenanthroline) for which a cubo-octahedral structure of the cluster core was found by transmission electron microscopy.[99]

Apparently the conclusions about the structure of the clusters reached on the basis of electron microscope studies should be treated with much caution. However, if the agglomeration or breakdown of metallic particles are not observed in the course of the electron microscope study, as happened in the case of the palladium cluster, then electron diffraction patterns can be used for the independent estimation of the particle sizes.

The size of the particles responsible for diffraction, estimated from the half-widths of the diffraction rings, is approximately 25 Å for the cluster (I), which agrees with electron microscope and small angle X-ray diffraction data (Fig. 5):

Method	d, Å
Electron microscopy	26±3.5
Electron diffraction	25
Small angle X-ray diffraction	20

The small angle X-ray diffraction data also indicate the virtually unimodal nature of the size distribution of the particles.

The packing of the palladium atoms in the metallic core of compound (I) was determined with the aid of EXAFS spectra.[94] The RDA curve obtained on the basis of these spectra has a peak which corresponds to a Pd–O (or Pd–N) distance of 2.1 ± 0.1 Å. Four intense peaks correspond to the shortest Pd–Pd distances (Table 2). The observed set of interatomic Pd–Pd distances agrees best with the eicosahedral packing of the palladium atoms in the metallic core of the cluster (I) (the expected interatomic distances between the nearest neighbouring atoms in the eicosahedron are in the proportions 1:1.2:1.4:1.6) and differs appreciably from the expected set of distances for the face-centred cubic and hexagonal close packing.

The average atomic volume of palladium in the eicosahedral metallic core of compound (I), calculated using the interatomic distances from Table 2, is approximately 16 Å^3, which exceeds only slightly the atomic volume for metallic palladium (14.7 Å^3). This result rules out the possibility of the coordination of the Phen and OAc ligands to the inner palladium atoms in the cluster. Consequently the Phen and OAc groups are arranged on the periphery of the metallic core of the cluster (I).

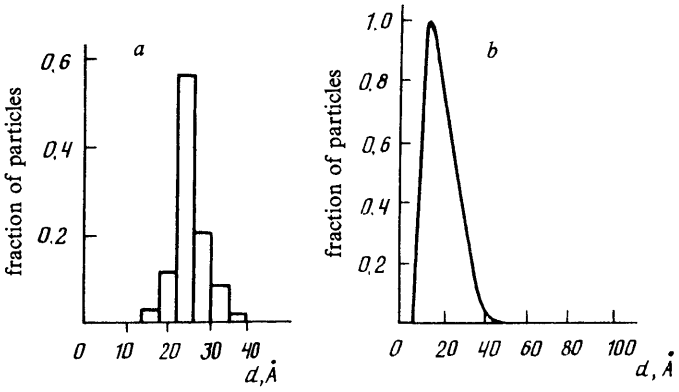


Figure 5. The size distribution of the metallic cores of the giant clusters (I) according to electron microscope (*a*) and small angle X-ray diffraction (*b*) data.

Table 2. Experimental (based on EXAFS data) shortest interatomic Pd–Pd distances in the metallic core of the cluster (I) and the values expected for different types of packing.

Type of data	Pd–Pd distance, Å				
Experimental	2.60±0.004	3.10±0.1	3.66±0.1	4.08±0.1	
Calculated for different types of packing:					
face-centred cubic	2.60		3.66		
hexagonal	2.60		3.66		4.50
eicosahedral	2.60	3.10	3.66	4.10	

Note. The smallest of the shortest distances was assumed to be 2.60 Å in the calculations for all types of packing.

Knowing the nature of the packing of the palladium atoms and the distances between the nearest neighbouring palladium atoms, it is possible to estimate the number of palladium atoms in the cluster molecule. For a sphere approximately 25 Å in diameter, this number N_Σ approximately equals 570. On the basis of this value and the chemical composition obtained from the results of elemental analysis, the molecule of compound (I) can be represented approximately by the formula $Pd_{570\pm30}Phen_{63\pm3}(OAc)_{190\pm10}$. The molecular weight corresponding to this formula (N = 83200) agrees with the result of the direct determination from the rate of sedimentation from aqueous solution.

The observed value $n = 570$ agrees well with the value of N_Σ for the idealised model comprising a 5-layer eicosahedron containing 561 metal atoms in conformity with the formula

$$N_\Sigma = {}^1/_3(10m^3+15m^2+11m+3) = 561 \quad [100],$$

where m is the number of eicosahedral layers ($m = 5$). Taking into account the chemical composition, the idealised formula $Pd_{561}Phen_{60}(OAc)_{180}$ was proposed for the eicosahedral cluster (I). This idealised formula apparently corresponds to the average size and composition of the cluster and not to definite fixed dimensions and chemical composition. In other words, the distribution of the particles of compound (I) about an average size $d \simeq 25$ Å and the idealised composition $Pd_{561}Phen_{60}(OAc)_{180}$.

This situation resembles to some extent organic polymers in which different molecules contain different numbers of monomeric units. Bearing in mind that the average Pd–Pd bond energy is fairly small (40–60 kJ mol^{-1}), one may expect that such giant clusters have certain defects ("apices", "niches", etc.) which are difficult to detect by electron microscopy.

Analysis of molecular models showed that the Phen ligands coordinated as bidentate species can be coordinated only at the apices and edges of the eicosahedron because of the steric hindrance generated by the H atoms in the 2- and 2'-positions in the *o*-phenanthroline molecule. As a result of this, out of the 252 metal atoms in the outer layer of the idealised eicosahedron only about 60 can be linked to the *o*-phenanthroline ligands involved in the bidentate coordination. The complete formal charge on the metallic core together with the electrically neutral Phen ligands is 180+ and is balanced by 180 anionic OAc^- ligands.

In this arrangement, almost the entire surface of the metallic core is sterically shielded by the bulky *o*-phenanthroline groups. The acetate anions can therefore be arranged only in the outer sphere of the cluster cation (I) (Fig. 6). We may note that a similar outer-sphere disposition of acetate anions was observed by X-ray diffraction in the tetranuclear cluster $[Pd_4Phen_4(CO)_2](OAc)_4$ [34] (Fig. 4).

The conclusion that the ligands OAc^- are involved in outer-sphere coordination was also confirmed by IR spectroscopic data [the frequency difference is $\nu_{as}(OCO)-\nu_s(OCO) = 165$ cm^{-1}, as in solid CH_3COONa] and ^1H NMR data (the line due to the protons of the OAc^- groups is observed as a narrow singlet at $\delta = 2.0$ p.p.m., in contrast to the appreciably broadened Phen multiplet).

The cluster (I) can be precipitated from aqueous solution by adding salts such as NaX or KX ($X^- = Cl^-$, Br^-, ClO_4^-, HSO_4^-, PF_6^-, AsF_6^-) with substitution of the OAc^- anions by X^-. Treatment of compound (I) with the salt KPF_6 yielded a cluster with the idealised formula $Pd_{561}Phen_{60}O_{60}(PF_6)_{60}$ (II), which is soluble in acetonitrile.[90,91]

Electron microscope data showed[91] that the metallic core of this cluster is almost spherical and has a diameter of 28 ± 5 Å, which agrees with small angle scattering data.

The results of chemical analysis and the stoichiometry of the conversion of the cluster (I) into (II) showed that the substitution of the outer-sphere OAc^- ligands in aqueous solution is accompanied by the partial hydrolysis of the cluster, as a result of which only 60 out of the 180 OAc^- anions are substituted by the PF_6^- anions, while the remaining 120 OAc^- anions are substituted by O^{2-}:[90]

$$Pd_{561}Phen_{60}(OAc)_{180}+60\,PF_6^-+60\,H_2O = Pd_{561}Phen_{60}(PF_6)_{60}O_{60}+ +120\,AcOH+60\,AcO^-.$$

Molecular clusters containing between 4 and 38 palladium atoms are known to be diamagnetic.[85,101] In contrast to this, the clusters (I) and (II), containing several hundreds of palladium atoms in the metallic core, possess metal-like properties, such as temperature-independent paramagnetism. The specific magnetic susceptibility at 300 K [$\chi_g^{300} = 1.0 \times 10^{-6}$ CGSU for (I) and 0.8×10^{-6} CGSU for (II)[90]] is close to that for metallic palladium particles deposited on SiO_2 [degree of dispersion 0.2–0.5; $\chi_g^{300} = (0.8 \pm 0.2) \times 10^{-6}$ CGSU[102]].

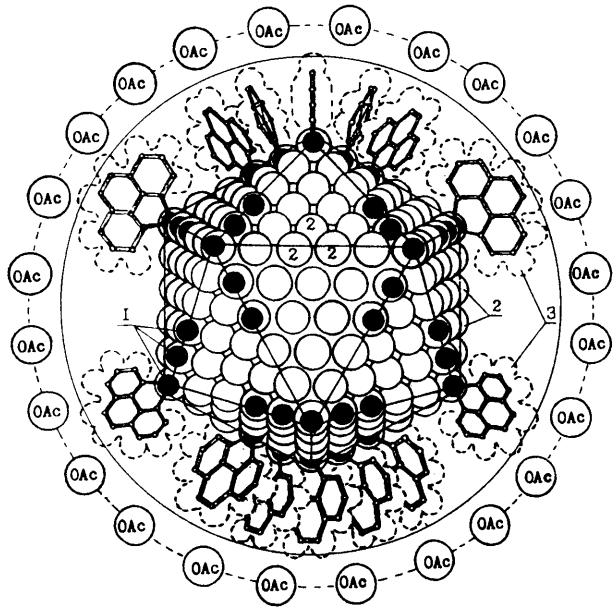


Figure 6. Idealised model of the giant cluster (I): *1*, palladium atoms coordinated to the phenanthroline ligand; *2*, palladium atoms available for coordination to the OAc^- anions or substrate molecules; *3*, van der Waals limits of the coordinated phenanthroline molecules.

The metallic core of the cluster (II) was also investigated by the EXAFS method.[90] The RDA curve for freshly prepared specimens of the cluster indicates the presence of Pd–Pd distances characteristic of both eicosahedral and cubo-octahedral cores. However, 30–100 days after the preparation of the specimen, only the peaks corresponding to a face-centred cubic lattice (cubo-octahedron) remain on the RDA curve. Similar changes in the structure of the metallic core were observed also after the replacement of the outer-sphere OAc^- anions by the BF_4^-, HSO_4^-, ClO_4^-, etc. anions. These data indicate the ease with which the eicosahedral packing of the metal atoms in the skeleton of the giant cluster relaxes to the cubo-octahedral packing as a result of the substitution of the ligands and standing for a long time even at room temperature.

Analysis of our molecular models showed that 60 oxygen atoms can be accommodated as bridging groups between the surface palladium atoms of the metallic core on the faces of a cubo-octahedron with a diameter of 28 Å without steric hindrance due to the 60 coordinated *o*-phenanthroline molecules.

The possibility of the coordination of oxygen atoms to the surface atoms of the metallic core in giant clusters was recently confirmed by the synthesis of a platinum cluster with the idealised formula $Pt_{309}L_{36}O_{30\pm10}$ (L = bis-sulphophenylphenanthroline),[99] which was obtained by the same method as the cluster (II) using platinum(+2) acetate instead of palladium(+2) acetate and a phenanthroline derivative in the form of the sodium salt of the corresponding sulphonic acid (see above). In the case of palladium, these investigators obtained a giant cluster with 561 palladium atoms in the idealised formula and a somewhat different composition of the coordination shell.[103]

The giant clusters obtained apparently serve as a bridge between the usual molecular clusters and colloidal metals. The size of the metallic core in giant clusters exceeds appreciably the size of the usual molecular clusters such as $Pd_{38}(CO)_{28}(PEt_3)_{12}$ [101] and $Au_{55}(PPh_3)_{12}Cl_6$,[104] approaching the lower limit of the sizes of colloidal metal particles. In contrast to the latter, giant clusters have a distinct ligand environment with a definite stoichiometry of the type characteristic of molecular clusters. However, in both cases when the number of metal atoms approaches several hundreds, a set of more or less imperfect metallopolyhedra is formed with a certain distribution with respect to size and chemical composition.

In principle, the metallic cores of such clusters need not necessarily contain the "magic number" of metal atoms.[100,105] Nevertheless large and giant clusters with metallic cores in the form of two-layer (M_{55}),[96] four-layer (M_{309}),[99] and five-layer (M_{561})[91] 12-vertex particles are now known.

Since the relaxation energy of the close packing is extremely small, such metallopolyhedra can readily undergo interconversions and, depending on the ligand environment, temperature, and other factors, can be stabilised as isomeric cubo-octahedra, eicosahedra, and anticubo-octahedra.[105] The solution of the problem of their true geometry requires the application of experimental methods, for example EXAFS, which do not have a destructive or some other strong effect on the substance.

The use of idealised formulae based on data obtained by the above methods is useful for the construction of models characterising the average size and composition of the giant clusters and suitable for the examination of their catalytic properties.

2. Catalytic properties of the giant clusters (I) and (II)

(a) Oxidative acetoxylation. In the presence of acetic acid in solutions of the clusters (I) and (II), oxidative acetoxylation reactions take place, involving the conversion of ethylene into vinyl acetate:

$$C_2H_4+{}^1/_2O_2+AcOH = CH_2{=}CHOAc+H_2O,$$

of propene into allyl acetate:

$$C_3H_6+{}^1/_2O_2+AcOH = CH_2{=}CHCH_2OAc+H_2O,$$

and of toluene into benzyl acetate:

$$PhCH_3+{}^1/_2O_2+AcOH = PhCH_2OAc+H_2O.$$

Their selectivity is 95–98%.[91] The only side reaction observed in the presence of these catalysts is further oxidation of the alkenyl and benzyl esters, as they accumulate, to ethylidene, allylidene, and benzylidene acetates respectively. Compared with metallic palladium catalysts, whose activity is manifested at higher temperatures,[106,107] the clusters (I) and (II) facilitate side reactions to a lesser extent.

(b) Oxidation of alcohols. The clusters (I) and (II) effectively catalyse the oxidation by molecular O_2 of primary aliphatic alcohols to esters in which the alcoholic and acid components have the same carbon skeleton as the initial alcohol:[108]

$$2RCH_2OH+O_2 = RCOOCH_2R+2H_2O.$$

Together with esters, the oxidation of primary alcohols leads to the formation of the aldehydes and the corresponding acetals (Table 3).

Secondary alcohols are smoothly oxidised to ketones:

$$(CH_3)_2CHOH+{}^1/_2O_2=(CH_3)_2CO+H_2O.$$

Table 3. Oxidation of alcohols by oxygen (1 atm) in the presence of the cluster (II) (suspension of 0.1 g of the cluster in 2.5 ml of the alcohol).

Alcohol	Temperature, °C	$10^3 W_0$, mol litre^{-1} h^{-1}	Composition of products	Yield, %
C_2H_5OH	60	2.3	$CH_3COOC_2H_5$	27
			$CH_3CH(OC_2H_5)_2$	55
			CH_3CHO	18
n-C_3H_7OH	60	2.0	$C_2H_5COOC_3H_7$	7
			$C_2H_5CH(OC_3H_7)_2$	16
			C_2H_5CHO	77
iso-C_3H_7OH	20	2.1	$(CH_3)_2CO$	100
n-C_4H_9OH	60	1.3	$C_3H_7COOC_4H_9$	59
			$C_3H_7CH(OC_4H_9)_2$	38
			C_3H_7CHO	3

(c) The formation of acetals from carbonyl compounds and alcohols. Presumably the oxidation of primary alcohols proceeds via the intermediate formation of aldehydes. This hypothesis is supported by the finding that, in the absence of O_2, acetaldehyde introduced into an alcoholic suspension of a cluster (II) is converted into the acetal:[109]

$$CH_3CHO+2EtOH=CH_3CH(OEt)_2+H_2O.$$

This reaction is of a general character and is catalysed not only by the clusters (I) and (II) but also by different types of palladium black.

(d) Oxidation of formic acid. The gas-phase decomposition of HCOOH into CO_2 and H_2 takes place at an appreciable rate on deposited palladium catalysts even at 50 °C.[110] The clusters (I) and (II) as well as palladium black catalyse the decomposition of HCOOH in the gas phase in the absence of O_2 at 50 °C. However, in the liquid phase at the same temperature the decomposition of HCOOH is not observed. In the presence of O_2 in solutions containing the clusters (I) and (II), formic acid is oxidised at 20–70 °C:[111]

$$HCOOH+{}^1/_2O_2=CO_2+H_2O.$$

In solutions of the clusters (I) and (II) in acetonitrile, the reaction kinetics are described by an equation of the Michaelis–Menten type:

$$W = k[\text{Clust}][\text{HCOOH}]\frac{[O_2]}{K + [O_2]}.$$

The observed isotope kinetic effects $k_{HCOOH}/k_{HCOOD} = 1.1 \pm 0.1$ and $k_{HCOOH}/k_{DCOOD} = 1.0 \pm 0.1$ show that the C–H and O–H bonds are not ruptured in either the rate-limiting or the preceding stages. A reaction mechanism was proposed on the basis of these data[111] in which the rate-limiting stage is the coordination of the undissociated HCOOH molecule to the palladium atoms on the surface of the metallic core. The subsequent stages—the dissociation of the coordinated HCOOH, the transfer of an H atom to the coordinated O_2, and the removal of the products from the surface of the metallic core of the cluster—are rapid and are not reflected in the reaction kinetics.

Thus giant palladium clusters exhibit a varied catalytic activity in both oxidation reactions and in the reactions which traditionally belong to the field of acid–basis catalysis. The mechanism of these reactions has been studied in greatest detail in relation to the oxidative acetoxylation of ethylene and propene.

VII. Kinetics and mechanisms of oxidation reactions in solutions of giant palladium clusters

The kinetics of the oxidation of ethylene in solutions of the cluster (II) in acetic acid–acetonitrile mixtures obey the following kinetic equation:[112]

$$r_0 = k[\text{Clust}]\frac{[C_2H_4]\cdot[O_2]\cdot[\text{AcOH}]}{(K_I + [C_2H_4])(K_{II} + [O_2])(K_{III} + [\text{AcOH}])},$$

where r_0 is the rate of formation of vinyl acetate from ethylene and K_I, K_{II}, and K_{III} are Michaelis constants.

The rate of accumulation of allyl acetate in the oxidation of propene in solutions of the clusters (I) and (II) is also directly proportional to the cluster concentration. In contrast to ethylene, deviations from linearity are not observed in the relation between r_0 and the propene concentration. However, when the O_2 concentration is varied, the rate of reaction changes in a more complex manner than was observed in the oxidation of ethylene. At a propene partial pressure greater than 0.9 atm, this variation is represented by a curve with a plateau, but, as the propene partial pressure is reduced to 0.5 atm, a maximum characteristic of the inhibition of the reaction by the initial reactant (in the given case oxygen) appears on the $r_0 = f(P_{O_2})$ curve. For $P_{C_3H_6} > 0.7$ atm, i.e. under conditions where the reaction is not inhibited by oxygen, the rate is described by an equation analogous to the kinetic equation for ethylene with the sole difference that the Michaelis constant for propene is much greater than that for ethylene (Table 4).[113] Comparison shows that the rate constants for the oxidation of ethylene and propene in the presence of both clusters differ by less than a factor of three. The range of variation of the Michaelis constants K_{II} and K_{III} on passing from one alkene to another and on replacing the cluster (I) by (II) is also not very great.

The greatest difference between the kinetic characteristics of the ethylene and propene oxidation reactions involves the appreciable alteration of the constant K_I.

The Michaelis nature of the kinetics of these reactions suggests that the oxidation-reduction reactions are preceded by stages involving the reversible coordination of the alkene, O_2, and AcOH to the cluster and that propene is coordinated much more weakly than ethylene, O_2, and AcOH.

In homogeneous alkene oxidation reactions with participation of mononuclear and dinuclear palladium(+2) complexes, the oxidation product is formed in the absence of O_2 in stoichiometric amounts relative to the palladium(+2) which has reacted. In contrast to this, in solutions of the clusters (I) and (II) the oxidation of alkenes in the absence of O_2 is not observed. This fact also indicates that the reactions of ethylene and propene in solutions of giant clusters cannot be explained by the alternation of oxidation-reduction reactions of the cluster with the substrate and the oxidant. The lower formation constants of the π-complexes of propene compared with ethylene can be accounted for by the greater size of the molecule of this substrate.

Table 4. Constants of the kinetic equation for the oxidation of ethylene and propene in solutions of the clusters (I) and (II) at 60 °C.

Substrate	Cluster	k, min^{-1}	K, mol $litre^{-1}$		
			$10^3 K_I$	$10^4 K_{II}$	K_{III}
Ethylene	(II)	8.2±0.7	5.8±0.3	3.0±0.2	1.3±0.1
Propene	(I)	3.3±0.3	30	5.2±0.3	0.67±0.05
Propene	(II)	5.6±0.5	30	1.2±0.1	4.8±0.5

Indeed, the surface of the metallic core of the cluster is sterically blocked by the bulky phenanthroline ligands. Analysis of the idealised molecular model showed that, on the surface of the metallic core of the cluster (I), there are approximately 20 palladium atoms sterically available for the coordination of the solvent or reactant molecules. However, the smaller C_2H_4 molecules are presumably coordinated more strongly at these sites than the C_3H_6 molecules whose steric requirements are more stringent. For the real molecules of a giant cluster, which probably differ to a greater or lesser extent from an ideal polyhedron, the number of accessible sites differs from that for the idealised model. This number can be determined experimentally by introducing into the solution of the cluster some kind of ligand (catalytic poison) which is strongly bound to the accessible palladium atoms on the surface of the metallic core. The results obtained for the influence of different poisons (Fig. 7) showed that ligands which are bulky (PPh_3, phenanthroline) but are effectively coordinated to palladium hardly affect the rate of oxidation of alkenes, since they do not apparently find on the surface of the cluster sites available for their coordination. Smaller ligands (mercaptans, thiocyanate, etc.) effectively block the cluster.

A similar picture has been observed also for the HCOOH oxidation reaction.[111] The complete inhibition of the ethylene oxidation reaction requires the blocking of approximately 50 palladium atoms, whereas for propene it is sufficient to bind only 15 metal atoms in the cluster to the poison ligand for the cluster to lose its catalytic activity.[112,113] These data confirm the above hypothesis that the steric factor plays a decisive role in the formation of complexes between the substrate and the cluster.

Oxidative alkene acetoxylation reactions reduce to the dissociation of the C–H bonds in the initial alkene and the substitution of the H atom by the OAc group. The kinetic data obtained have shown, however, that in solutions of the giant clusters both reactions take place at similar rates despite the considerable differences between the strengths of the C–H bonds in ethylene (the strength of the vinyl–H bond is 106 ± 2 kcal) and in propene (the strength of the allyl–H bond is 86.2 ± 2 kcal) (see Ref. 114, p. 39). This finding shows that, despite the common form of the kinetic equation, the rate-limiting states in the ethylene and propene reactions are significantly different. This hypothesis is supported by the kinetic isotope effects obtained (Table 5).[91]

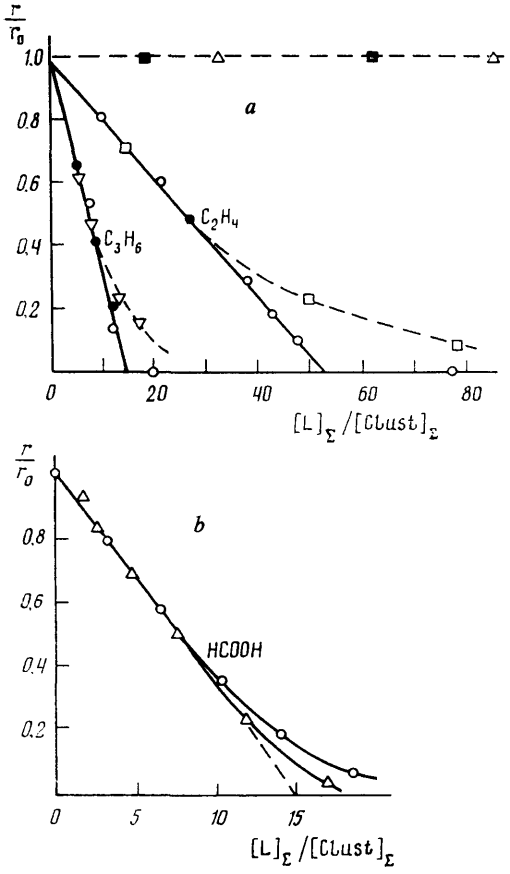
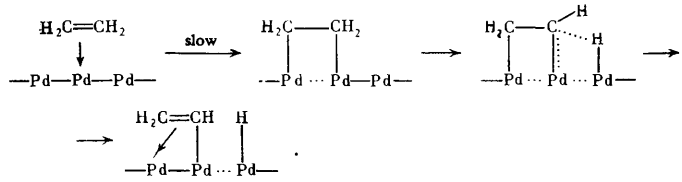


Figure 7. Dependence of the relative rates of oxidation of alkenes (*a*) and formic acid (*b*) by oxygen in solutions of the giant cluster (II) on the concentration of ligand-inhibitors: *a*, ○—$(C_2H_5)_2NCS_2Na$; ●—C_2H_5SH; ▽—I_2; □—KSCN; Δ—Phen; ■—PPh_3. *b*, ○—NaSCN; Δ—$(C_2H_5)_2NCS_2Na$.

In the ethylene molecule, the C=C π-bond is weakest (~60 kcal). The data in Table 5 are consistent with the fact that hydrogen atoms are transferred from the coordinated C_2H_4 and CH_3COOH molecules in rapid stages following the rate-limiting stage. The closeness of the isotope effect H/D for ethylene to unity can be explained by the fact that in the slow stage the π-coordinated C_2H_4 molecule undergoes oxidative addition (with opening of the C=C π-bond) to the Pd–Pd group of the cluster with formation of the σ,σ-coordinated group...Pd–CH_2CH_2–Pd...:

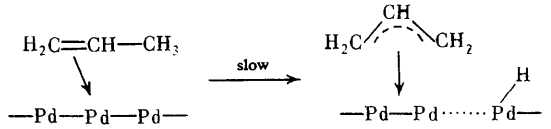


One cannot rule out the possibility that the subsequent dissociation of the C–H bond in this group is facilitated because of the possibility of the formation of a Pd–C multiple bond in the transition state.[115]

Analogous forms of adsorption had been postulated earlier for the hydrogenation and dehydrogenation of ethylene and the H/D exchange involving it on the surfaces of metallic catalysts.[116] Reliable evidence for the formation of σ,σ-coordinated ethylene and a π,σ-coordinated vinyl group on the surface of Pd(100) was obtained recently by means of a combination of thermoprogrammed reaction spectroscopy (TPRS) and high-resolution electron energy loss spectroscopy (HREELS).[117]

The intermediate formation of σ-bound organopalladium compounds $XPdCH_2CH_2OR$ had been established earlier in reactions involving the oxidation of ethylene by palladium(+2) salts.[118] In the case of the giant clusters (I) and (II), the palladium atoms at the metallic core of the cluster in an oxidation state close to zero participate in the reaction; as a result of the formation of the σ,σ-complex, the formal oxidation state of each of these atoms increases by unity, returning to the initial oxidation state after the completion of the catalytic cycle.

In the case of propene, the difference between the strengths of the π-C=C and allyl–H bonds is much smaller than the difference between the energies of the π-C=C and vinyl–H bonds in ethylene. The insertion of propene in the Pd–Pd bond of the cluster with dissociation of the allyl–H bond probably leads to a π-allyl complex and a coordinated hydride:



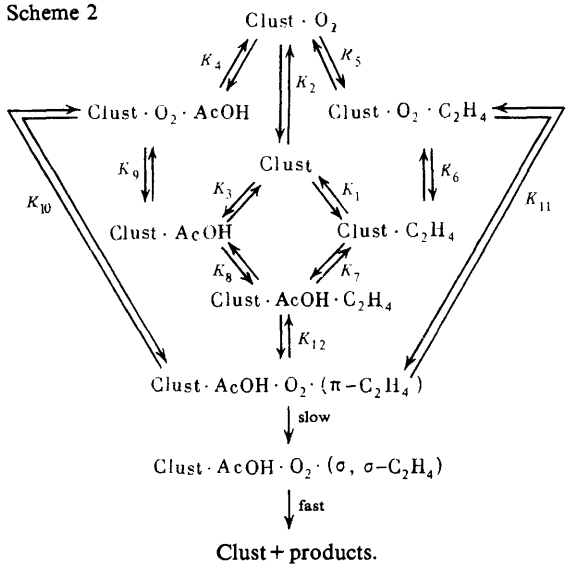
The stabilisation of the π-allyl complex as a result of the formation of a surface π-allyl group probably favours the situation where the competition between the vinyl and allyl reaction pathways is won by the latter and the oxidative acetoxylation of propene on clusters (I) and (II) proceeds only via the allyl pathway. The experimental kinetic isotope effects are consistent with the scheme (Table 5).

Table 5. Kinetic isotope effects in the oxidation of ethylene and propene by oxygen in solutions of the clusters (I) and (II) at 60 °C.

Substrate	Cluster	$k_{C_nH_{2n}}/k_{C_nD_{2n}}$	$k_{CH_3COOH}/k_{CD_3COOD}$
Ethylene	(II)	1.1±0.1	1.1±0.1
Propene	(I)	2.2±0.2	1.0±0.05
Propene	(II)	3.6±0.2	1.0±0.05

The subsequent reactions of the coordinated vinyl and allyl groups and H atoms on the surface of the metallic core of the cluster are apparently rapid and are not reflected in the rates of the overall reactions (see Scheme 2).

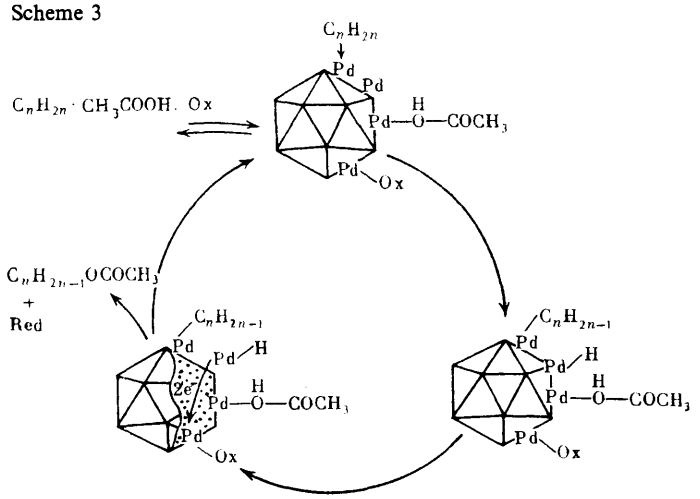
Scheme 2



The data for the inhibition of the alkene and HCOOH oxidation reactions by ligands[91,111] showed that only about 20% of the surface palladium atoms are accessible to the reactant molecules in the oxidation of ethylene and only about 5–6% of the total number of these atoms are accessible in the oxidation of propene and formic acid. It is unlikely that on the surface of the metallic core of the cluster shielded to such an extent all three molecules—O_2, the substrate undergoing oxidation, and AcOH—would be coordinated to neighbouring palladium atoms of the same section of the cluster. Apparently there are better grounds for the expectation that the alkene or HCOOH molecule is bound to one section of the cluster, the O_2 molecule is coordinated to another, not necessarily neighbouring, section, and electron transfer from the Pd–alkenyl, Pd–formyl, or Pd–H fragment to the coordinated O_2 molecule proceeds via the metallic core of the cluster, which plays the role of an "electronic mediator".[31]

The overall reaction scheme can be represented as follows:

Scheme 3



Not only O_2 but also palladium(+2) salts can function as electron acceptors in cluster catalytic systems. Thus propene is oxidised to allyl acetate in the stoichiometric reaction of C_3H_6 with $Pd(OCOCH_3)_2$ in CH_3COOH. The particles of dispersed metallic palladium, formed in the initial period of this reaction, can then play the role of the cluster catalysing the allyl oxidation of propene.[119] This approach makes it possible to explain the previously observed[68,120] change in the selectivity of the reaction of palladium(+2) with propene in acetic acid. For a comparatively small change in conditions (temperature, AcONa concentration, H_2O, added oxidants), the yield of allyl acetate varies from 4 to approximately 90%.

In the presence of the clusters (I) and (II), benzoyl peroxide can also serve as the electron acceptor. Thus in solution in acetic acid containing the clusters (I) and (II), the reaction

$$C_3H_6 + (C_6H_5COO)_2 + CH_3COOH = CH_2{=}CHCH_2OCOCH_3 + 2C_6H_5COOH,$$

takes place at 20 °C with a selectivity of 98–100% with respect to allyl acetate.[121]

Although outwardly this reaction looks like peroxide oxidation, it proceeds fundamentally via the same mechanism as the oxidation by oxygen or palladium(+2) on clusters, in the absence of which the reaction does not occur under the conditions indicated.

VIII. Conclusion

Thirty years ago, the oxidative metal complex catalysis was represented by mainly free-radical processes. Against the background of this extensive class of reactions, the molecular oxidation of alkenes in solutions of palladium salts, where the unsaturated substrate encounters neither oxygen nor its partial reduction products, appeared to be a glaring exception. Nowadays oxidation reactions without the participation of free radicals occupy a due place both in the arsenal of industrial chemistry and in laboratory practice.

The field of molecular oxidative catalysis has been continuously developing. Together with complexes containing metal atoms in stable oxidation states, cluster compounds containing metal atoms in unusual oxidation states begin to be used in catalytic practice. The application of metal complexes made it possible to generate singlet oxygen and ozone from hydrogen peroxide. The coordination compounds responsible for these reactions contain ligands in which the oxygen atoms have unusually low fractional oxidation states. Apparently, as metal complex catalysis develops, chemists will encounter increasingly new examples of unusual oxidation states of both the central atoms and the ligand atoms. We suggest that the advances in metal complex catalysis and in coordination chemistry are in many respects inter-related and depend on the interaction of these two branches of chemical science.

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Metal complexes of macrocycles in catalysis

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ABSTRACT. The reactions catalysed by metal complexes with synthetic macrocyclic ligands and, in particular, the hydrolysis reactions of esters, peptides, and other substrates are examined. Many macrocyclic coordination compounds of transition metals are active catalysts of reactions occurring at electrodes (electrocatalysis). The catalysis by macrocyclic transition metal compounds of reactions involving the oxidation of various organic substances by molecular oxygen and other oxidants, in particular, the oxygen compounds of the halogens, is described. Examples of photocatalysis with participation of macrocyclic transition metal complexes as catalysts are presented. Certain features of the electronic structure of transition metal complexes with macrocyclic ligands are considered and routes leading to further development of catalysis using such compounds are outlined.

The bibliography includes 90 references.

Contents

I.	Introduction	1150
II.	Characteristic features of metal complexes of macrocycles important for catalysis	1150
III.	Catalysis of hydrolytic reactions by macrocyclic metal complexes	1152
IV.	Electrocatalytic reactions with participation of macrocyclic metal complexes	1152
V.	Reactions involving oxidation by oxygen catalysed by macrocyclic metal complexes	1153
VI.	Other reactions catalysed by macrocyclic metal complexes	1154
VII.	Conclusion	1155

I. Introduction

Although the first systematic studies on the synthesis and properties of metal complexes of macrocyclic compounds were not carried out until the 1960s, the number of compounds of this kind described at the present time runs to several thousand. Studies on the synthesis and physicochemical characteristic of macrocyclic complexes have been surveyed in a number of monographs.[1–4]

Comparatively few studies have been devoted to the catalytic acceleration of various reactions by macrocyclic compounds but their number has increased sharply during the last decade. A general feature is manifested here: after the discovery and study of a new class of chemical compounds, their application begins to develop vigorously. This was the case, for example, with complexones and metal complexonates, which are now finding extensive applications in various branches of the national economy.

It is noteworthy that, as early as the 1970s, catalytic reactions with participation of natural macrocyclic compounds such as the porphyrins and phthalocyanines, a kind of analogue of the former, were investigated vigorously. Since a number of monographs and reviews have been devoted to this question,[5–7] the reactions catalysed by metalloporphyrins and metallophthalocyanines will not be considered as a rule in the present review. Nor will the extremely specific field of the so called phase transfer catalysis be considered. In it macrocyclic compounds (mainly crown-ethers) play the role of an agent transferring the reactive substance from one phase to another (for further details, see Hiraoka[2]).

II. Characteristic features of metal complexes of macrocycles important for catalysis

Solvated (including hydrated) metal ions can participate in many catalytic processes by themselves. Nevertheless, the incorporation of a metal ion in the cavity of a macrocycle alters its properties extremely significantly. A metal ion in a macrocyclic environment is in the first place fully or partly desolvated (dehydrated). On partial desolvation, the possibility of a fairly easy replacement of the remaining solvent molecules by the ions or molecules of the catalytic reaction substrate appears. In this case, the metal ion can function as an acid centre ("Lewis acid") and can also catalyse hydrolytic reactions such as hydrolysis, solvolysis, etc. Here one may see a certain analogy with hydrolytic enzymes such as carboxypeptidase and carbonic anhydrase, which contain in their active centres a zinc ion surrounded by electron-donating oxygen atoms of carboxylic acids or nitrogen atoms of imidazole groups. Zinc, copper, cobalt (II) and (III), and many other metal ions characterised by a marked tendency to combine with nucleophilic species can play the role of acid centres.

The electron-donating atoms of the macrocyclic ligand, coordinated in a specific way around the central metal atom, create a ligand field characterised by a definite "strength", expressed, for example, by the spectrochemical parameter $10Dg$ in an octahedral complex. Several electron-donating ligand atoms are fairly frequently arranged in approximately the same equatorial plane, leaving the axial positions relatively free for the substrate molecules or ions and one may therefore speak of the axial coordination of the substrate molecule or ion.

The possibility of such coordination is determined by the electronic structure of the central ion. For example, in the case of low-spin nickel(II) complexes the axial coordination of the substrate is difficult owing to the presence of the electron pair in the axially oriented d_{z^2} orbital and, conversely, in complexes with an unoccupied d_{z^2} orbital the σ-type axial coordination of a substrate species is entirely possible [low-spin macrocyclic iron(II), cobalt(III), etc. complexes]. The appearance of a dative π-bond of the type

LM(II)→S may play a major role in the formation of intermediate compounds of the substrate and the macrocyclic complex.

The oxidation-reduction potential of the M(n+1)L/M(n)L couple depends on the nature of the electron-donating atoms and other characteristics of the macrocyclic ligand (L). [8] The redox potential is determined by the potential of the simple solvated ions M(n+1) and M(n) and by the ratio of the stability constants of the complexes M(n)L and M(n+1)L. The greater this ratio (we shall designate it by η), the higher the redox potential of the given pair of complexes and conversely.

Among the factors which determine the ratio η, the following may be specified.

1. The nature of the electron-donating atoms in the macrocycle: the highest η is characteristic of ligands with sulphide sulphur atoms and the lowest of ligands with ether oxygen. Ligands with electron-donating amine nitrogen atoms have intermediate values of η.

2. The charge on the ligands: the ratio η diminishes with increase in the negative charge of L.

3. The size of the cavity within the macrocycle: η also increases with increase in the size of the cavity.

4. The possibility of the formation of dative π-bonds from the metal to the macrocycle leads as a rule to an increase in η.

Apart from these factors, it is essential to take into account the change in the spin state on oxidation-reduction of the complex, the difference between the effects of the ligand field on the M(n) and M(n+1) ions, the presence of alkyl substituents in the macrocycle, the change in the symmetry of the field on passing from M(n)L to M(n+1)L, etc.

By selecting the macrocyclic environment, it is possible to regulate the redox potential of the M(n+1)L/M(n)L couple which catalyses the oxidation-reduction process at a particular stage of the latter.

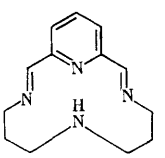
The possibility of the axial coordination of a nucleophilic molecule in the presence of an equatorial ligand and an unoccupied d_{z^2} orbital was noted above. If this orbital is occupied by a pair of electrons, the corresponding macrocyclic complex is itself converted into a nucleophile capable of combining with a proton, carbonium ions (for example, CH_3^+), and other "electrophiles". Such addition must not be hindered by a high positive charge on the complex and the nucleophiles are therefore usually macrocyclic cobalt(I) and nickel(I) complexes bearing low charges and having an unshared electron pair in the d_{z^2} orbital.

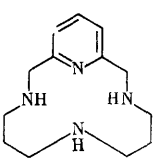
When the d_{z^2} orbital, oriented at right angles to the xy plane in which the electron-donating atoms of the macrocyclic ligand are located, is half-filled and six electrons are present in the d_{xz}, d_{yz} and d_{xy} orbitals (d^7 configuration), a kind of inorganic free radical species are produced [Co(II)L, Ni(III)L], which are capable of reacting with free radicals or generating them as a result of the homologous bond dissociation in the organic molecule.

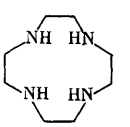
The characteristic features of the macrocyclic complexes of metal ions considered here make it possible not only to explain the mechanism of many catalytic processes but also to predict new ones. Even greater possibilities for the prediction of catalytic reactions with participation of macrocyclic complexes have arisen from the far-reaching analysis of processes in enzyme catalysis[9] and the construction on this basis of the corresponding models of the active centres of the enzymes. [10,11]

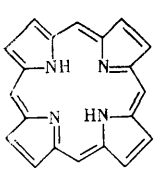
The use of the analogy between the active centres of metalloenzymes and a metal ion with its immediate environment in a complex ML, where L is a macrocyclic ligand, made it possible to discover many catalytically active compounds. In particular, using metalloporphyrins as analogues of haems and metallocorrins, it has been possible to achieve numerous catalytic processes in which metalloporphyrins and metallophthalocyanines are used. [5,6]

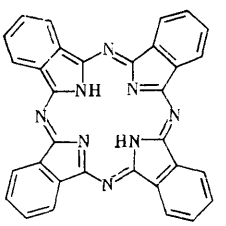
Despite the fact that several thousands of macrocyclic compounds are known nowadays, complexes with an extremely limited number of ligands (several tens) are used in catalytic reactions. In the further exposition in this review, we shall use structural formulae and the corresponding numbering of the ligands in considering the latter:

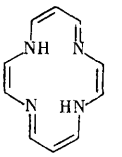

L1 (CR)

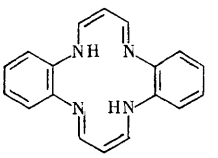

L2 (CRH)

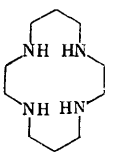

L3 (cyclene)

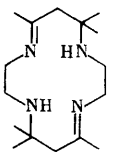

L4 (H_2P)

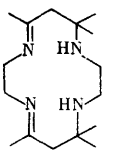

L5 (H_2Pc)

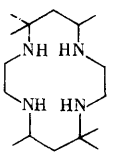

L6 (H_2TAA)

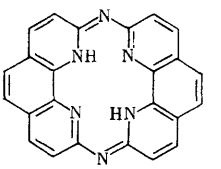

L7 (H_2DBTAA)

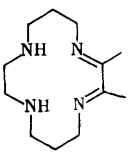

L8 (cyclam)

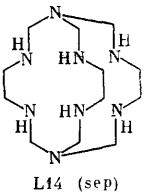

L9 (td)

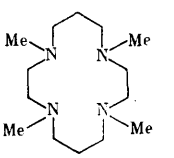

L10 (cd)

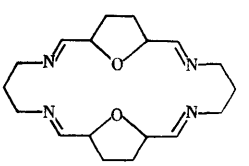

L11 (teta)

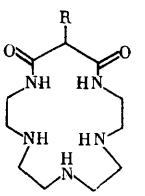

H_2L12

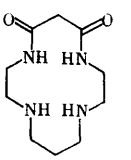

L13

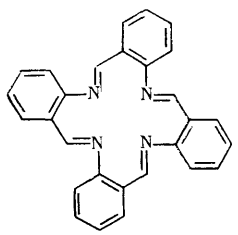

L14 (sep)


L15 (TMC)

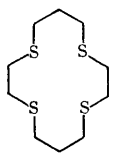

L16


H_2L17

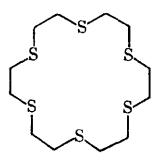

H_2L18



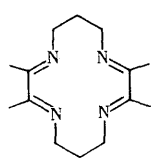
L19 (TAAB)



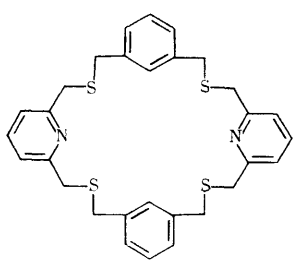
L20 (Ref.12 an S_4)



L21 (Ref.18 an S_6)



L22 (TIM)



L23

At the same time, use will be made of the conventional abbreviations for many ligands used widely in Soviet and foreign scientific literature. The ligands not illustrated here will be named in accordance with the Melson-Bush nomenclature,[1,3] which has come to be widely employed in the Soviet and foreign literature.

III. Catalysis of hydrolytic reactions by macrocyclic metal complexes

Many hydrolytic reactions (hydrolysis of peptides, esters, etc.) are catalysed by zinc-containing enzymes (for example, carboxypeptidase). The active centres of such enzymes contain a zinc ion linked to the electron-donating nitrogen atoms of the imidazole groups of histidine or the electron-donating oxygen atoms of the carboxy-groups of the glutamic acid residues. The complex $Zn(CR)^{2+}$ or ZnL1,[12] which accelerates the hydrolysis of methyl trifluoroacetate according to the scheme

$$CF_3COOMe+OH^- = CF_3COO^- + MeOH\ ,$$

by a factor of 6, can be considered as a model of this active centre.

The acceleration can be explained by the formation of a bond between the hydroxide ion and the zinc ion in the macrocyclic complex, as a result of which OH^- acquires the ability to add to the carbon atom of the ester group. The same complex $Zn(CR)^{2+}$ catalyses the hydration of acetaldehyde, i.e.

$$MeCHO+H_2O = MeCH(OH)_2\ ,$$

and the analogous CO_2 hydration reaction catalysed by carbonic anhydrase.[13] The substitution of zinc by copper(II) in the complex $M(CR)^{2+}$ increases its catalytic activity, in contrast to carbonic anhydrase. The catalytic activity of $M(CR)^{2+}$ [13] is due to the fact that it ensures the addition of the metal-coordinated hydroxide ion to the carbon atom in CO_2 or MeCHO at pH close to the physiological values.

The complexes $Zn(CR)^{2+}$ also catalyse the hydrolytic reactions of many phosphate esters, which is important as a detoxification procedure.[14] The catalytic reactions

$$(PhO)_2P(O)OC_6H_4NO_2+H_2O = (PhO)_2P(O)OH+NO_2C_6H_4OH,$$

and

$$(PhO)_2P(O)OC_6H_4NO_2+H_2O =$$

$$= (PhO)P(O)(OC_6H_4NO_2)OH+PhOH,$$

which proceed in a mixture of water and acetonitrile, have been described. The proposed mechanism of these reactions is analogous to that described above.

Similar hydrolytic reactions are catalysed not only by the complexes $Zn(CR)^{2+}$ but also by $Zn(cyclene)^{2+}$ (cyclene = L3).[15] $Zn(cyclene)^{2+}$ is even more effective than $Zn(CR)^{2+}$ in the hydrolysis of the ester $(NO_2)_2C_6H_3OP(X)(O)OEt$ (where X = Me or OEt).

The macrocyclic zinc complex $Zn([15]anN_4)^{2+}$ catalyses the hydrolysis of 4-nitrophenyl acetate.[16]

The cobalt(III) complex $[Co(cyclene)(H_2O)_2]^{3+}$ accelerates the hydrolysis of ATP with formation of ADP and phosphate.[17] The catalytic activity of this complex is manifested particularly strikingly at pH 8.6 (acceleration by a factor of 117), at pH 8.0 the ratio of the rate constants for the catalytic and non-catalytic reactions is 13.2, while at pH 7.0 it is only 2.2.

It has been suggested that cobalt(II) complexes with a chiral macrocycle containing the cyclene skeleton be used for the selective hydrolysis of specific N-terminal groups of peptides and for the conversion of L-alanine.[18]

IV. Electrocatalytic reactions with participation of macrocyclic metal complexes

Numerous studies devoted to the application of macrocyclic compounds in electrocatalysis are known. The earliest investigations concern the use of metalloporphyrins and metallophthalocyanines for the reduction of molecular oxygen at the cathode of a fuel cell.[19] Reviews of studies on this question are available in a number of monographs[5,6,20] and in a communication.[21]

The reduction of molecular oxygen at the cathode of a fuel cell is described by the overall equation[22]

$$O_2+4H^+ + 4e = 2H_2O,\ E^0 = 1.229\ V.$$

However, the process is complicated by intermediate reactions and, in particular, by the reduction of oxygen to hydrogen peroxide, which is characterised by a lower redox potential:[22]

$$O_2+2H^+ + 2e = H_2O_2,\ E^0 = 0.695\ V.$$

Other intermediate reactions in the reduction of O_2 to H_2O are also possible. Catalysis of the above overall reaction and of its individual stages is therefore necessary. The salts MPc and the salts of substituted porphyrins MP, especially cobalt(II), iron(II), and iron(III) salts, are used as catalysts. This is apparently associated with the ease of the formation of superoxide radical-anions O_2^- in the presence of the above complexes and their subsequent conversion into H_2O_2. It was subsequently observed that the salts of tetraazaannulenes (MTAA and MDBTAA) also exhibit a catalytic activity[23,24] these compounds being actually more active than the porphyrin and phthalocyanine salts. It may be that the salts of porphyrins, phthalocyanine and tetraazaannulenes also possess catalase activity, i.e. they accelerate the conversion of H_2O_2 into H_2O and O_2.

Studies on cobalt salts of different substituted tetraazannulenes[25] showed that the presence of various alkyl substituents in these compounds does not have a significant effect on the electrocatalytic activity of CoTAA.

Other cobalt salts of tetraaazamacrocyclic ligands [$Co(cyclam)^{3+}$, $Co(td)^{2+}$], forming intermediate dinuclear complexes with oxygen, have also been investigated as electrochemical reduction catalysts.[26] The cobalt complex with the hexaazamacrocyclic ligand L12 likewise proved to be a catalyst of the electrochemical reduction of molecular oxygen.[27]

Carbon electrodes modified by cobalt and iron salts with natural and synthetic polyazamacrocyclic ligands do not lose their activity on pyrolysis (600–800 °C). The latter actually increases.[27–33] It is naturally unlikely that the initial cobalt complexes were retained at the electrode.

The electrochemical reduction of oxygen to hydrogen peroxide at a rotating disc electrode is catalysed by the tetraazamacrocyclic cobalt complexes of cyclam (L8) or td (L9).[26] The ions $Co(cyclam)^{2+}$ also accelerate the subsequent reduction of H_2O_2 to H_2O when the conditions are altered.[34]

The electrochemical CO_2 reduction reactions, catalysed by macrocyclic coordination compounds, are of great theoretical and practical interest. Carbon dioxide is the main participant in photosynthetic reactions and in the future it may become the starting material for organic synthesis. Finally, the utilisation of CO_2 constitutes an extremely important aspect of the solution of ecological problems.

The most important electrochemical CO_2 reduction reactions are listed below with an indication of the corresponding standard potentials in an acid medium[22]:

$$CO_2 + 2H^+ + 2e = CO + H_2O,\ E^0 = -0.106\ V,$$

$$H_2CO_3 + 2H^+ + 2e = HCOOH + H_2O,\ E^0 = -0.166\ V,$$

$$2H_2CO_3 + 2H^+ + 2e = H_2C_2O_4 + 2H_2O,\ E^0 = -0.391\ V,$$

$$H_2CO_3 + 4H^+ + 4e = HCHO + 2H_2O,\ E^0 = -0.050\ V.$$

In an alkaline medium, the same reactions are characterised by different standard potentials[22]:

$$CO_3^{2-} + 3H^+ + 2e = HCO_2^- + H_2O,\ E^0 = 0.310\ V,$$

$$2CO_3^{2-} + 4H^+ + 2e = C_2O_4^{2-} + 2H_2O,\ E^0 = 0.478\ V,$$

$$CO_3^{2-} + 6H^+ + 4e = HCHO + 2H_2O,\ E^0 = 0.197\ V.$$

It is seen from the data presented that the electrochemical reduction of CO_2 can lead to the formation of a set of different products (CO, HCOOH, $H_2C_2O_4$, etc.).

Electrochemical CO_2 reduction reactions are accelerated by cobalt and nickel complexes of porphyrin and phthalocyanine[5,6,20] and also by cobalt complexes with comparatively simple tetraazamacrocyclic ligands.[35] Cobalt complexes with the "transdiene" (L9), the dimethyl-*cis*-diene (L13), and CR (L1), as well as nickel (II) complexes of CR (L1) have been investigated as catalysts of this chemical process.[36] A mechanism was proposed for the reduction of CO_2 to the final products (CO, HCOOH, $H_2C_2O_4$) and for the formation of hydrogen as a result of the reduction of the water protons (in all cases, cobalt is linked to the macrocyclic ligand):

$$\begin{array}{ccccc} Co\,(II) & \overset{+e}{\rightarrow} & Co^{-}(I) & \xrightarrow{+H^+} & Co\,(III)\,(H^-) \xrightarrow{+H^+} Co\,(III) + H_2 \\ & & \uparrow\downarrow{\scriptstyle +CO_2} & & \uparrow\downarrow{\scriptstyle +CO_2} \\ & & Co\,(I)\,CO_2 & & Co\,(III)\,(HCO_2^-) \overset{+H^+}{\rightleftarrows} Co\,(III) + CO + H_2O \\ & & \uparrow\downarrow & & \uparrow\downarrow{\scriptstyle +H^+} \\ & & Co\,(III) + C_2O_4^{2-} & & Co\,(III) + HCOOH\ . \end{array}$$

The electrocatalysis was carried out at a mercury cathode.

Further studies showed that nickel(II) complexes of cyclam (L8) exhibit an especially high effectiveness and selectivity in the reduction of CO_2.[37] Subsequently the mechanism of the electrochemical reduction of CO_2 was investigated in fair detail.[38]

It was established that the complex $Ni(cyclam)CO^+$ as well as the compounds $LNi(III)CO_2$ and LNi(II)CO may be formed as intermediates in the electrocatalytic reduction of CO_2.[39] The electrochemical reduction of carbon dioxide has also been observed at electrodes with a polymeric coating containing nickel complexes of tetraazaannulenes (L6, L7, etc.).[40]

The study of CO_2 as a ligand is of special interest.[41] Certain coordination compounds of cobalt(I), containing tetraazamacrocyclic compounds and carbon dioxide as ligands, have been described and characterised quantitatively.[42,43]

The bimacrocyclic cobalt complex $Co(sep)^{3+}$ (CoL14) [44] and the nickel complex $Ni(teta)^{2+}$ (NiL11) are used in electrocatalytic hydrogen evolution reactions.[45]

The electrocatalytic reduction of nitrate at a mercury electrode with formation of hydroxylamine, proceeding in accordance with the equation

$$NO_3^- + 7H^+ + 6e = NH_2OH + 2H_2O,$$

has been described.[46] The reaction is catalysed by nickel(II) and cobalt(III) complexes of cyclam (L8). The complexes of other transition metals with this ligand have a low activity.

Transition metal complexes with macrocyclic ligands also catalyse many electrochemical (anodic) oxidation processes. For example, cobalt complexes of porphyrins, phthalocyanine, and tetraaza-annulenes (L6, L7) catalyse the anodic oxidation of $SO_2(H_2SO_3)$, whereas copper, nickel, and palladium complexes are catalytically inactive.[47] The catalytic activity of the tetraazamacrocyclic complexes diminishes in the sequence CoTAA ≫ CoTPhP > CoPc. The catalytic activity of carbon electrodes modified by CoTAA persists also after their pyrolysis at 800 °C.[48]

The tetraazamacrocyclic nickel complex NiL18 catalyses the anodic oxidation of benzyl alcohol to benzaldehyde; the formation of the compound Ni(III)L as an intermediate is then postulated.[49] The same reaction is catalysed by the ruthenium(IV) and ruthenium(V) complexes of tetramethylcyclam (L15).[50]

Finally, the anodic oxidation of $PhSCH_2Si(Me)_3$ in the presence of an alcohol ROH leads to the formation of $PhSCH_2OR$ and the $Si(Me)_3^+$ cations:[51]

$$PhSCH_2Si\,(Me)_3 \xrightarrow{ROH} PhSCH_2OR + Si\,(Me)_3^+ + H^+ + 2e.$$

V. Reactions involving oxidation by oxygen catalysed by macrocyclic metal complexes

Catalysis by tetraazamacrocyclic transition metal complexes M(teta) and M(td) of the reactions involving the oxidation of various substrates, in particular cyclohexene, by molecular oxygen

has long been known.[52] The oxidation reactions of hydrogen sulphide and various mercaptans, catalysed by porphyrin complexes of cobalt, iron, copper, nickel, and a number of other transition metals, have been described.[5,6] To some extent, a similar catalytic activity of macrocyclic dinuclear complexes of copper(I) and copper(II) of the type Cu_2L (L = L16) is manifested in the reactions[53,54]

$$2\,PhSH + {}^1/_2\,O_2 = PhSSPh + H_2O,$$
$$2\,PhC{\equiv}CH + {}^1/_2\,O_2 = PhC{\equiv}C{-}C{\equiv}Ph + H_2O,$$
$$PhNHNHPh + {}^1/_2\,O_2 = PhN{=}NPh + H_2O.$$

Dinuclear complexes of the type Cu_2L16 can be regarded as models of the active centres of certain copper oxidases containing the so called EPR-undetectable copper(III).

Nickel complexes with a kind of tetraazamacrocyclic ligand-anions, each containing two amide (peptide) groups (L17, L18), exhibit a high catalytic activity in reactions involving the oxidation of various substrates by molecular oxygen. These nickel complexes catalyse the oxidation of benzene to phenol, of toluene to cresol, etc.[55,56] and also the oxidation of styrene by oxygen in the presence of tetrahydroborate.[57]

The catalytic acceleration of the oxidation of 1,3-bicyclooxolan to ethylene glycol monoformate by cobalt(II) complexes of dibenzo-18-crown-6 [58] appears fairly unexpected since cobalt(II) complexes do not form any kind of stable complexes with crown-ethers.

The copper(I) and copper(II) complexes with the tetraazamacrocyclic ligand TAAB (L19) catalyse the oxidation of ascorbic acid by molecular oxygen.[59,60] Ascorbic acid free radicals and superoxide radical-anions are then formed. Under certain conditions, this reaction can proceed in the vibrational regime.[61] Tetraazaannulene complexes of iron catalyse the oxidation of hydroquinone to quinone in solution in pyridine.[62]

Finally, the oxidation of a number of alcohols to aldehydes and ketones is catalysed by thiamacrocyclic complexes of copper(II) (L20 and L21). The copper compounds of the type $CuL20^{2+}$ and $CuL21^{2+}$ can be regarded as analogues of the active centres of the so called "blue proteins".[63]

Macrocyclic complexes of transition metals catalyse the photochemical oxidation of methanol to formaldehyde. Iron(II) complexes with the tetraazamacrocyclic ligand TIM (L22)[64] as well as the cobalt(III) complexes with the ligands L9 (td) and L14 (sep) [65,66] can be used as catalysts.

VI. Other reactions catalysed by macrocyclic metal complexes

The analogy between haem-containing proteins—catalase and peroxidases—and tetraazamacrocyclic transition metal complexes suggested that the latter might exhibit catalase or peroxidase activity. Such activity has been observed in iron(III)-, cobalt(III)-, ruthenium(III)-, and osmium(IV)-pthalocyanines.[67] Somewhat later, it was established that the complex $[Fe(CRH)Cl_2]^+$ (CRH = L2) possesses catalase activity.[68] The activity of $[Fe(CRH)Cl_2]^+$ is an order of magnitude smaller than that of catalase but an order of magnitude higher than that of the iron(III) aquo-ion. Subsequently it was discovered that this iron complex exhibits a peroxidase activity in the oxidation of benzene and its substituted derivatives by hydrogen peroxide.[69] The iron(II) complex of TAAB (L19) does not exhibit an appreciable catalase activity but it does possess a pronounced peroxidase activity: in its presence, hydrogen peroxide oxidises a number of substrates. The oxidation of the dye Eriochrome Black has been characterised quantitatively.[70]

Cobalt(II) complexes of sepulchrates (sep = L14) reduce oxygen quantitatively to H_2O_2, being oxidised at the same time to $Co(sep)^{3+}$, which subsequently readily returns to the initial state $Co(sep)^{2+}$.[71]

The complexes NiL17 and NiL18 exhibit a superoxide dismutase activity.[72]

A number of reactions with participation of NaClO and PhIO as oxidants are accelerated by nickel(II) complexes of cyclam (L8) and chelating ligands (salen).[73] If $NaClO_4$ is used for the oxidation of alkenes, the catalytic activity of the macrocyclic complex is then found to be lower than that of the complexes of Schiff bases, while in the case where PhIO is employed the nickel complex of cyclam is found to be a more effective catalyst. The PhIO oxidant converts styrene and *trans*-stilbene into benzaldehyde and styrene epoxide in the presence of the dinuclear copper complex Cu_2L_{23}.[74]

The epoxidation reaction is also catalysed by nickel complexes of cyclam and its substituted derivatives, especially TMC (L15).[75] The proposed mechanism of the catalysis of the epoxidation of alkenes in the presence of nickel complexes of cyclam postulates the formation of intermediate nickel(III) or even nickel(IV) compounds. Cobalt(II) complexes of cyclam exhibit a weak catalytic activity and the $Cu(cyclam)^{2+}$ complex is altogether inactive.[76] Nickel complexes of the tetraazamacrocycles CR (L1) and TIM (L22) also possess a high catalytic activity in epoxidation reactions.[77] The catalytic acceleration of the oxidation of styrene with formation of the epoxide and benzaldehyde by the iron(III) complex of a 21-membered chiral macrocyclic ligand, containing four amide and one bipyridyl group, has been observed.[78]

A characteristic feature of the vast majority of vibrational chemical reactions is the involvement in the oxidation of the substrate (for example, malonic acid) by an oxidant (for example, bromate) of a transition metal compound as catalyst in which the metal undergoes a periodic change in the oxidation state. Such a compound may be, in particular, a macrocyclic complex.[79]

It has been observed that tetraazamacrocyclic copper(II) complexes catalyse the oxidation of malonic acid by bromate in an oscillating reaction. The oxidation state of the copper then changes from 2 to 3 and back again. The use of copper(II) complexes with teta, td, and cd (L11, L9, and L10 respectively) as catalysts has been examined.[80–83] The copper complexes with unsaturated ligands (td and cd) can, in contrast to the complex with the saturated ligand (teta), function not only as catalysts but also as substrates, i.e. the ligands cd and td can be oxidised by bromate in the vibrational mode. A similar picture is also observed when nickel complexes of the *cis*-diene cd (L10) are used as catalysts.[81–83]

The use of metal complexes with macrocyclic ligands for the catalytic acceleration of chain transfer from polymers to the monomer in radical polymerisation reactions has been examined in a number of studies. Low-spin cobalt(II) complexes with tetraazamacrocyclic ligands, in particular, with porphyrin and derivatives of tetraazaannulenes (L4, L6, L7), exhibit a catalytic activity, while cobalt complexes of td, teta, and TAAB (L9, L11, and L19 respectively) are inactive.[5,7,84] In the key stage, the radical-like compound Co(II)L reacts with hydrogen atom of the substrate and forms a radical and a cobalt hydride of the type $(H^-)Co(III)L$. This hydride then decomposes with elimination of hydrogen, while the cobalt returns to the initial state cobalt(II).

Photocatalytic reactions involving the evolution of hydrogen from water on treatment with various electron donors, photosensitisers,

and photocatalysts have been described. Cobalt(II) sepulchrates (the L14 ligand) can be used as photocatalysts.[44,85] The use of the complex $Ni(cyclam)^{2+}$ in the photocatalytic evolution of H_2 from water in a system containing a bipyridylruthenium complex (sensitiser) and ascorbic acid (electron donor) has been described.[86] It is suggested that the nickel(II) in the macrocyclic complex is reduced to Ni(I)L; this nickel(I) compound, which possesses nucleophilic properties, reacts with a proton to form the complex $(H^-)Ni(III)L$, which evolves H_2 on reaction with protons and is reduced by ascorbic acid to Ni(II)L (L = cyclam).

Even earlier, it was shown that the photocatalyst of the water reduction reaction in solutions containing bipyridylruthenium complexes as the sensitiser and europium(II) salts as the electron donor may be the cobalt complex of TIM (L22).[87]

Coordination compounds of nickel(II) with chiral macrocyclic ligands, containing sulphide sulphur in the macrocycle or amine nitrogen as well as sulphur, catalyse Grignard reactions[88,89] and, in particular, the reaction between RMgCl and vinyl bromide.

VII. Conclusion

Catalysis by metal complexes with macrocyclic ligands constitutes a new chapter in chemical science, more than 90% of the studies quoted in the literature referring to the last decade. The considerable unutilised possibilities of this field of study are indicated by the fact that, out of the several thousand macrocyclic ligands described, only a few tens, most thoroughly investigated and readily synthesised, have so far found applications in catalysis. The possibility of using macrocyclic coordination compounds to model the activity of many metalloenzymes opens the way to good future prospects. Studies of this kind are associated with the development of a new promising scientific field — biomimetic chemistry ("biomimetics"),[90] particularly that aspect of it which deals with the creation of "synzymes" (synthetic enzymes).

Macrocyclic coordination compounds are used mainly in the catalysis of oxidation-reduction processes, although a certain number of hydrolytic reactions catalysed by metal complexes of macrocycles are known. In the case of oxidation-reduction processes, the possibility of regulating the redox potentials of catalysts within wide limits by varying the parameters of the macrocyclic ligand (the size of the cavity, the number and nature of electron-donating atoms, their positions, etc.) plays an extremely significant role. The possibility of detecting "unusual" electronic states of metal ions, including radical forms [low-spin cobalt(II) and nickel(III) complexes] and nucleophiles with an unshared electron pair located on the metal atom is of great importance. Finally, the possibility of varying the geometry and the electronic structure of the ligand itself from the "usual" macroheterocyclic cyclam (L8) to a complex system with a large number of π-bonds of the type of porphyrin or phthalocyanine gives rise to good future prospects.

Studies in the field of catalysis by metal complexes of macrocycles have so far been limited to a comparatively small number of metals. The extension of the range of metals incorporated in the macrocycle for the preparation of catalytically active species can lead to new results.

Finally, we may note that the application of metal complexes of macrocycles in catalysis is associated with the solution of a series of scientific-technical problems of very great current interest, such as the creation of fuel cells, the use of solar energy, the utilisation of CO_2, etc.

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Catalysis by metal complexes in organoaluminium synthesis

U M Dzhemilev, O S Vostrikova, G A Tolstikov

ABSTRACT. In this review a summary is given of studies conducted both within and outside the Soviet Union on the synthesis and conversions of organoaluminium compounds (OACs) in the presence of metal complexes as catalysts. The following reactions have been examined: catalytic hydro-, carbo- and cyclo-alumination of unsaturated compounds, cross-coupling and conjugate addition of OACs to enones, and certain other conversions of OACs in the presence of metal complexes as catalysts.

The bibliography includes 211 references.

Contents

I.	Introduction	1157
II.	Hydroalumination	1157
III.	Carbo- and cyclo-alumination	1160
IV.	Catalytic cross-coupling with organoaluminium compounds	1166
V.	Catalytic reactions of organoaluminium compounds with carbonyl-containing compounds	1168
VI.	Catalytic reactions across the aluminium-heteroatom bond	1169
VII.	Other catalytic reactions involving organoaluminium compounds	1170

I. Introduction

In contrast with organomagnesium compounds, which have been widely used in organic synthesis since their discovery by Grignard, organoaluminium compounds (OACs) were almost unknown up to the 1950s. Since then, in spite of their cheapness and the availability of simple derivatives, they have been used mainly as components in catalytic systems for oligo- and poly-merisation of olefins.

In recent years the position has changed as many OACs have been elevated to a position of importance in organic synthesis and laboratory practise, in spite of the fairly high risks associated with their handling. Thus, *i*-Bu_2AlH is now one of the most widely used reducing agents in organic synthesis; the effective use of OACs as selective alkylating agents also deserves a special mention.

The new opportunities for using OACs in organic synthesis are now more and more associated with catalysis by metal complexes. Their selectivity has led to the discovery of many hitherto unknown reactions of practical value, and the mild conditions under which they can be conducted have minimised handling risks. Some reactions uncharacteristic of OACs have also led to the preparation of novel reagents considered previously as 'exotic'. During the last 10–15 years, a significant growth in publications in this area has been recorded.

In this review there is a survey of the results obtained by using homogeneous metal complexes as catalysts in the synthesis of varied OACs and their subsequent reactions; information has been excluded on the use of OACs as components of catalytic systems for the oligo- and poly-merisation of unsaturated compounds.

II. Hydroalumination

Hydroalumination of unsaturated compounds is one of the most characteristic reactions of OACs and frequently applied[1]. It is more than 25 years ago that the first experiments in hydroalumination with complex metal catalysts were undertaken with a view to broadening the scope of the reaction.[2,3] Since then, a large number of publications and patents have appeared in which many transition metals have been proposed as hydroalumination catalysts. However, as a result of exhaustive studies in this area by Ashby et al.[4–6], it has been established that both hydrometallation and hydrogenation of the unsaturation can take place in the presence of low-valent transition metal complexes, the latter course arising by hydride transfer from the medium. Thus, at the present time, any report on catalytic hydrometallation is greeted with much scepticism if there is no supporting evidence over and above analytical data on the products of hydrolysis of the reaction mass. It is our opinion that, nowadays, only titanium and zirconium compounds are 'beyond reproach' as hydroalumination catalysts. However, in this review there will be an examination of several interesting conversions in the presence of other transition metal complexes where the formation of OACs has been reliably confirmed.

1. Hydroalumination of acetylenes

Hydroalumination of disubstituted acetylenes is relatively facile, and can be achieved under fairly mild conditions with the aid of *i*-Bu_3Al or *i*-Bu_2AlH in the absence of any catalyst; however, it is not possible to avoid unwanted side reactions or subsequent conversions of the formed vinylalanes.[1,7]

A catalytic amount of $Ni(acac)_2$ enhances the reaction of OACs with 4-octyne, phenylpropyne and certain other disubstituted acetylenes at 25 °C.[8] At the same time, titanium or zirconium complexes have no effect on this reaction.[9,10]

However, in the presence of Cp_2TiCl_2, complexes of *i*-Bu_3Al with organomagnesium compounds (*i*-BuMgBr, EtMgBr) hydroaluminate the majority of disubstituted acetylenes readily under mild conditions, thereby avoiding unwanted reactions.[9–11]

$$R^1C{\equiv}CR^2 + n\ i\text{-}Bu_3Al.RMgBr \xrightarrow[0-20\ ^\circ C,\ 20\ min]{Cp_2TiCl_2(2\%),\ Et_2O}$$

$$\rightarrow \underset{95-98\%}{\overset{M}{\underset{R^1}{\overset{|}{\diagup}}\!\!=\!\!\underset{R^2}{\diagdown}}} \xrightarrow{D_2O} \underset{100\%\ (Z\text{-isomer})}{\overset{D}{\underset{R^1}{\overset{|}{\diagup}}\!\!=\!\!\underset{R^2}{\diagdown}}}$$

R^1, R^2 = Alk, Ar, OR^3, $SiMe_3$; $n = 3-10$;

M = organomagnesium or organoaluminium compound.

The stereoselectivity with this reagent is as high as that with 9-borabicyclo[3.3.1]nonane, and there is no difference in regioselectivity for the hydrometallation of unsymmetrically disubstituted acetylenes.

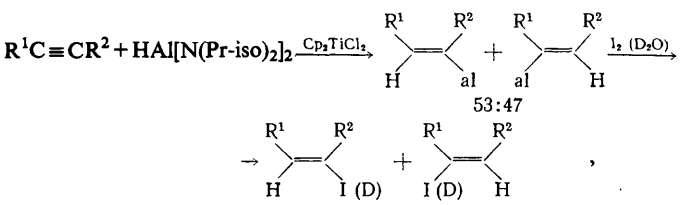
In the carboalumination of monosubstituted acetylenes with triethyl- and tripropyl-aluminium,[12-13] there is little mention of catalytic hydroalumination as a side reaction, and no indication on the possibility of achieving selective hydroalumination.

There are numerous examples of hydroalumination of acetylenes with a variety of complex hydrides. For this purpose, Ashby[14] recommended the novel bis(dialkylamino)alanes, being prepared in quantitative yield by interaction of aluminium with *sec*-amines under hydrogen pressure:

$$Al + H_2 + 2\,R_2NH \xrightarrow[\text{benzene}]{140\ ^\circ C,\ \sim 140\ atm\ H_2} HAl(NR_2)_2, \quad 100\%$$

R = Pr, Bu, Am.

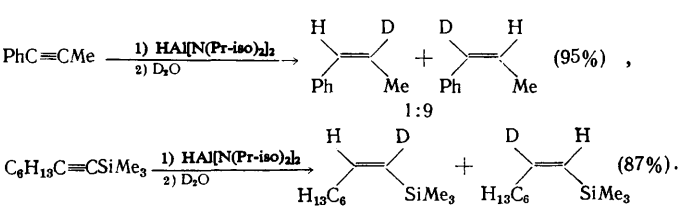
In the presence of 5 mol% Cp_2TiCl_2, these hydrides readily add to mono- and di-substituted acetylenes in benzene (in which they are very soluble) at 0 °C to room temperature.[15] The conversion of the acetylenes is nearly quantitative. (*Z*)-Alkenylalanes (90–96%) are the main products, the corresponding (*E*)-isomers being formed in no more 1–4% yield.



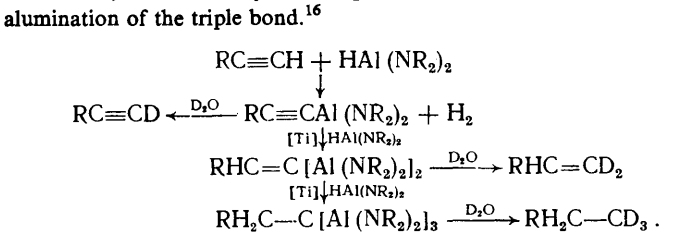
R^1 = Me, R^2 = n-Pr, al – organoaluminium compound.

Subsequent treatment with D_2O led to 96–97% incorporation of deuterium into the derived alkenes. The corresponding alkanes are formed simultaneously in up to 10% yield[16].

High regioselectivity is recorded only for the hydrometallation of 1-phenylprop-1-yne and 1-(trimethylsilyl)oct-1-yne:



For monosubstituted alkynes, deuterolysis of the products of hydroalumination affords, principally, a mixture of alkenes and alkanes in approximately equal amount with varying levels of D-incorporation; this confirms the complex nature of the metallation, and notably the aspect of mono- and di-hydroalumination of the triple bond.[16]



Hydroalumination of disubstituted acetylenes with other complex hydrides ($LiAlH_4$, $LiAlH_2[N(Pr\text{-}i)_2]_2$, $NaAlH_2(NEt_2)_2$, $NaAlH_2[N(Pr\text{-}i)_2]_2$, $LiAlMe_3H$) in the presence of Cp_2TiCl_2 or other titanium reagents proceeds in much the same way, the only difference being that stereoselectivity is higher (in some cases up to 100%) than with bis(dialkylamino)alanes and that side reactions are less.[5,6,16-19]

Mono- and di-phenyl-substituted acetylenes undergo hydroalumination non-selectivity, a significant amount of (*E*)-alkenylalanes being formed.[19]

2. Hydroalumination of olefins

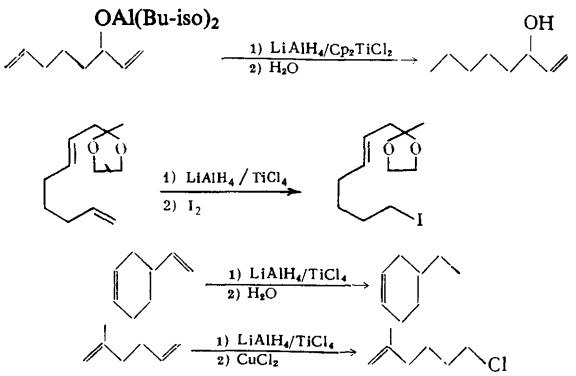
Catalytic hydroalumination of olefins is widely used in organic synthesis for a variety of purposes: for selective reduction of double bonds or their functionalisation, as well as for the preparation of higher OACs of defined structure for subsequent conversions.[20] Almost all of the readily available aluminium hydrides and simple alkylalanes have been used as hydroaluminating agents. For such purposes, $LiAlH_4$ has been most frequently used. Since Sato discovered that titanium and zirconium compounds may be used as catalysts for hydroalumination of olefins under mild conditions,[21,22] this reaction has found widespread application.

A variety of titanium complexes, among which those immobilised on inorganic[23] or polymeric[23,24] supports, is currently available for catalysed hydroalumination. The preliminary report[25] on the successful application of V and Cr salts as catalysts has not been subsequently confirmed. Recently, there was a communication[26] on the use of exotic catalysts, such as uranium salts (UCl_3 and UCl_4), for the hydroalumination of C_2–C_8 α-olefins. Zirconium complexes are no less effective than titanium complexes as catalysts; they are used preferably for the hydroalumination of allylic alcohols and ethers[27] since deoxygenation of these substrates takes place in the presence of titanium complexes.

It is reported[7,23,28] that reaction proceeds via intermediate formation of titanium or zirconium hydride complexes, which initially hydrometallate the olefin and are regenerated by subsequent transmetallation of the formed transition metal alkyl derivatives.

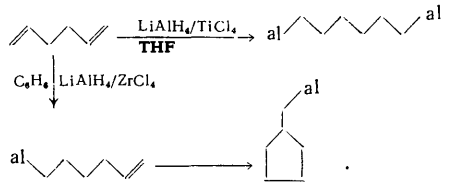
$$LiAlH_4 + ML_m \rightarrow L_nM{-}H,$$
$$L_nM{-}H + CH_2{=}CH{-}R \rightarrow L_nMCH_2{-}CH_2{-}R,$$
$$L_nMCH_2{-}CH_2{-}R + LiAlH_4 \rightarrow L_nM{-}H + al{-}CH_2{-}CH_2{-}R,$$
$$M = Ti, Zr;\ al = LiAl/4.$$

The relative reactivity of the alkenes in these reactions depends largely on steric factors. Disubstituted alkenes react far more slowly than monosubstituted alkenes, which in certain cases facilitates selective hydroalumination of the less substituted double bond:



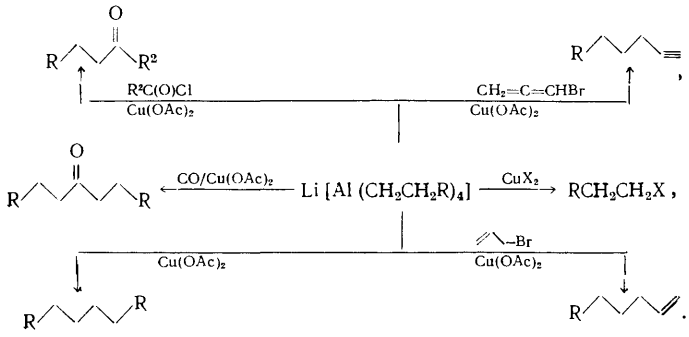
The course of the reaction with unconjugated α,ω-dienes, notably with 1,5-hexadiene, depends on the nature of the catalyst and the

reaction conditions. Thus, by using $TiCl_4$ in THF, 1,5-hexadiene was converted into acyclic bis-OACs; however, on replacement of THF by benzene, or of $TiCl_4$ by $ZrCl_4$, intramolecular cyclisation takes place:[9,15]



By catalytic hydroalumination a variety of highly reactive lithium tetralkylaluminates can be obtained, including derivatives with *O*- and *N*-functional groups.[27,30,33] Scheme 1 illustrates certain of their conversions in the presence of copper salts.[34–41]

Scheme 1



Such complex hydrides as $NaAlH_4$, $LiAlMe_3H$, $NaAlMe_3H$, and $NaAl(OCH_2CH_2OCH_3)_2H_2$ are no less active than $LiAlH_4$ in this respect.[6]

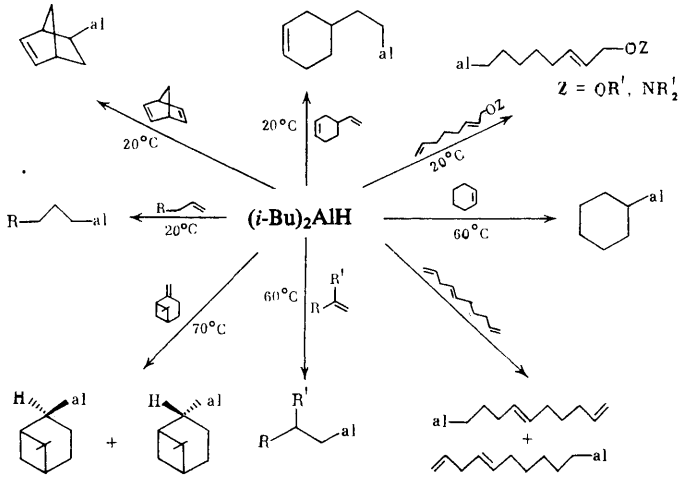
At the same time, other hydrides which Ashby studied, e.g. $HAl[N(Pr\text{-}i)_2]_2$, $HAl(NEt_2)_2$, $HAl[N(SiMe_3)_2]_2$, H_2AlCl, and $HAlCl_2$, displayed somewhat lower activity on hydroalumination of α-olefins in the presence of titanium complexes. As indicated above, the corresponding zirconium complexes exert almost no catalytic effect on the reaction.[4]

It has been reported that catalytic hydroalumination of conjugated dienes, e.g. isoprene, butadiene, and 1,3-hexadiene, can be achieved with $HAl[N(Pr\text{-}i)_2]_2$. However, selectivity in these reactions is not high.[4,23]

The more accessible and inexpensive alkylalanes may be used in place of complex hydrides for synthetically viable hydroaluminations. For hydroalumination of olefins with $(i\text{-}Bu)_2AlH$ under mild conditions, the most effective catalysts are zirconium salts;[42] with titanium catalysts, however, isomerisation and oligomerisation of the olefins are noted side reactions.

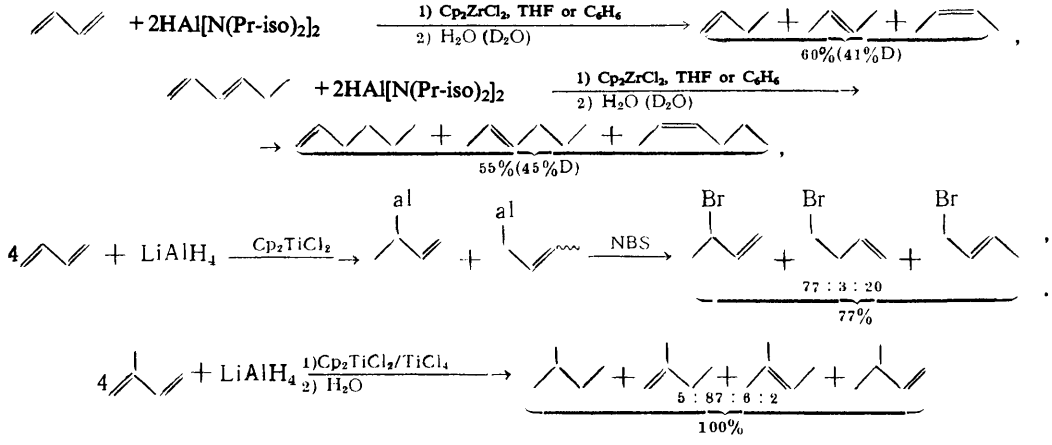
Thus, hydroalumination of α-olefins and norbornene derivatives with $(i\text{-}Bu)_2AlH$ can be effected almost quantitatively in the presence of $ZrCl_4$ at 20 °C during 3–6 h; the same reaction with α,β- and β,β′-disubstituted olefin requires a higher temperature (*ca.* 60 °C), thereby facilitating selective hydroalumination of polyene hydrocarbons possessing double bonds with different degrees of unsaturation (Scheme 2).[43–46]

Scheme 2



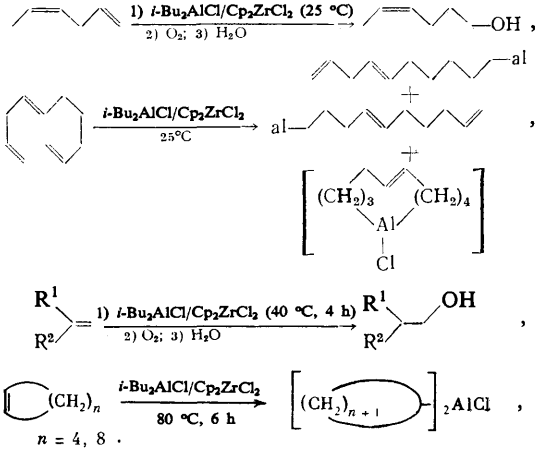
Chlorozirconium alkoxides have proved to be the most effective catalysts for hydroalumination of cyclic olefins.[44] The rate of hydroalumination of cyclic olefins depends on the ring size and decreases in the order: $C_5 > C_6 > C_7 > C_{12} > C_8$.

$i\text{-}Bu_3Al$ and $i\text{-}Bu_2AlCl$ are effective for the hydroalumination of a variety of olefins in the presence of a catalytic amount of Cp_2ZrCl_2.[47–50] $i\text{-}Bu_3Al$ adds to α-olefins even at 0–20 °C, which permits the synthesis of higher OACs under mild conditions; these include derivatives with functional groups (OH, SPh, Br) [47].

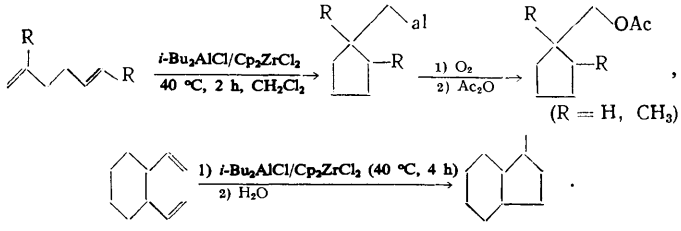


The interaction of *i*-Bu_3Al with cyclic olefins takes place at > 80 °C, although it is not possible to introduce more than two of the three isobutyl groups.[50]

Catalytic hydroalumination with *i*-Bu_2AlCl affords higher dialkylaluminium chlorides which cannot be obtained by classical routes, i.e. by non-catalytic hydroalumination.[48,50,51] For this reaction a general rule has been established: for hydroalumination with *i*-Bu_2AlH, α-olefins react most readily (at 25 °C), the disubstituted unsaturation in linear olefins reacts at 40 °C, and cyclic olefins only participate in reaction at 80 °C and above.

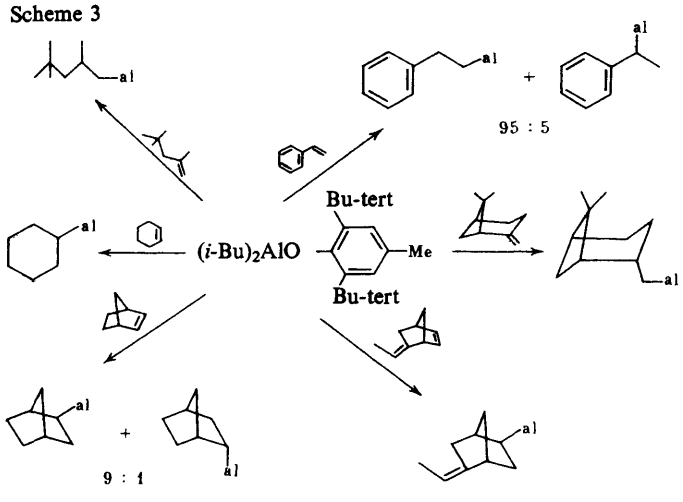


The interaction of 1,5-dienes with *i*-Bu_2AlCl under these same conditions leads to the formation of cyclic products:

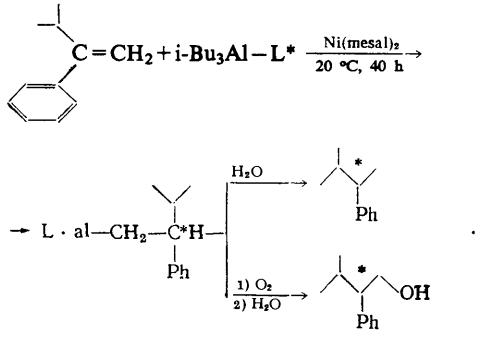


The organoaluminium monoaroxide obtained by interaction of *i*-Bu_2AlH with 2,6-di-tert-butyl-4-methylphenol regioselectively hydroaluminates mono- and di-substituted olefins (among which certain norbornene derivatives) at > 140 °C in xylene in the presence of *i*-Bu_2AlH/Cp_2ZrCl_2 as catalyst (Scheme 3).[52]

Scheme 3

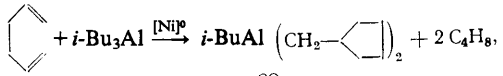


The asymmetric hydroalumination of prochiral alkenes with complexes of the type *i*-Bu_3Al-L^* (where L^* is an optically active amine, such as (–)-N,N-dimenthylmethylamine) is catalysed by $Ni(mesal)_2$ (where mesal is methyl salicylate):



Hydrolysis or oxidation of the formed alane yields the corresponding optically active hydrocarbon or alcohol with a maximum optical yield of 27% [53] and 67% [54], respectively. The possibility of regenerating the chiral base affords this method real potential in synthetic chemistry.

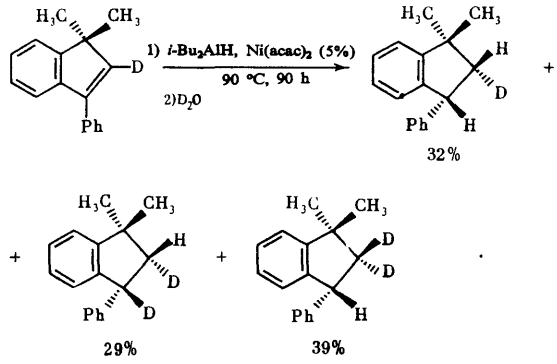
The use of zero-valent nickel complexes as catalysts for the hydroalumination of α-olefins with *i*-Bu_3Al permits the removal of the nickel catalyst as volatile $Ni(CO)_4$ at the end of the reaction; the higher OACs thus obtained do not contain catalytic impurities.[54]



$$[Ni]_0 \xrightarrow{CO} Ni(CO)_4,$$

$[Ni]^0 = (C_2H_4)_3Ni,\ (COD)_2Ni,\ (PhCH{=}CHPh)_3Ni.$

A recent systematic study of the mechanism of nickel-catalysed hydroalumination has revealed that there are general features in common with a mechanism involving hydride transfer. Experimental data confirms the fact that there are catalytically active intermediates, most notably bimetallic nickel-aluminium hydrides[55].



As a rule a significant amount of saturated products is formed in addition to OACs.

III. Carbo- and cyclo-alumination

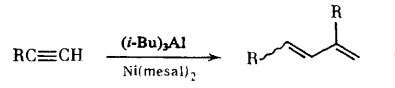
Stereo- and regio-selective single-step addition (i.e. monocarbometallation) of organometallic compounds to olefins and acetylenes is extremely important in synthetic planning since it leads to the

simultaneous formation of a metal–carbon and carbon–carbon bond. Although various metals are known to participate in the carbometallation of multiple bonds, only zirconium-catalysed carboalumination and cuprate synthesis by the Normant procedure permits the desired addition with high regio- and stereo-selectivity.

1. Carboalumination of acetylenes

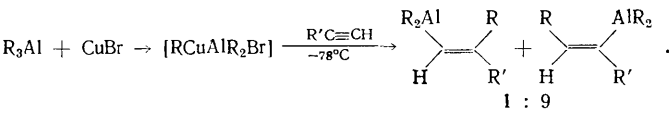
Non-catalytic carboalumination of mono- and di-substituted acetylenes is rarely applied in synthetic chemistry because of the low selectivity[7]. However, the number of transition metals which have been used as catalysts for this reaction is extremely large.

Attempts at selective carbometallation of monosubstituted acetylenes in the presence of Ni and Mn have proved to be effectively negative. Thus, treatment of mono-substituted acetylenes with i-Bu_3Al in the presence of $Ni(mesal)_2$ led to the formation of dimers:



Under the same conditions enynes gave a more complex mixture containing a small amount of product derived by hydro- and carbometallation, in addition to di- and tri-mers.[56–59]

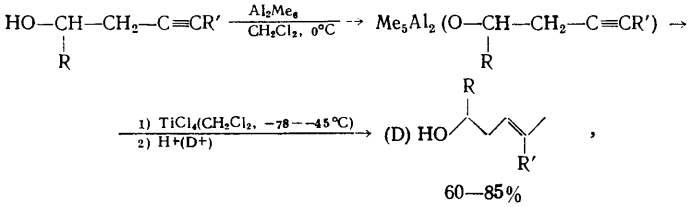
Carboalumination of 1-alkynes with trialkylalanes in the presence of $Cu(acac)_2$ and Ph_3P (Al : Cu : P = 2 : 1 : 1) is accompanied by their polymerisation, which leads to a reduction in the yield of desired product. High yields (up to 80%) and ⩾90% selectivity were found only by interaction of 1-alkynes with bimetallic aluminocuprate reagents, $R_3Al-CuBr$.[60,61]



1 : 9

Disubstituted acetylenes, propargyl and homopropargyl alcohol, as well as ether derivatives thereof, were shown to be inactive under these reaction conditions.

More promising results were obtained by using titanium-containing catalysts which in certain cases lead to high regio- and stereo-selectivity. However, this reaction also has a number of limitations. The best results are obtained for the carbometallation of the relatively accessible homopropargyl alcohols on treatment with Me_3Al in the presence of $TiCl_4$.[62,63]

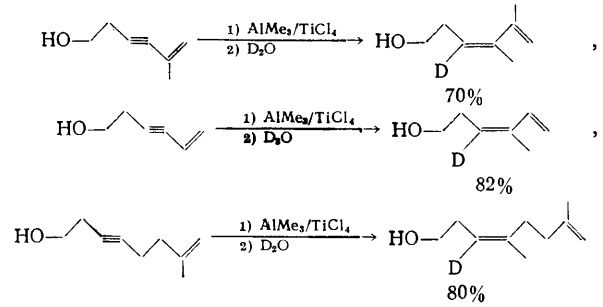


60–85%

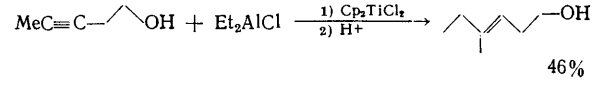
R = H, Me, Et, Ph; R′ = H, Me, Et, n-Pr, i-Pr, n-Bu, n-Am, Ph.

All the homopropargyl alcohols shown in the above scheme are selectively methylated at the triply-bonded carbon atom which is furthest from the OH-group.

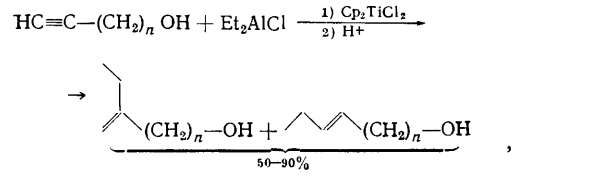
In the case of 5-en-3-yn-1-ols, reaction affords (3Z)-4-methylalka-3,5-dien-1-ols in high yield and with complete selectivity; here also the methyl group is exclusively on the C_4 atom.[64]



By replacement of Me_3Al by Et_2AlCl or $EtAlCl_2$, the level of regioselectivity is the same only in the case of disubstituted alkynes[65,66], the stereoselectivity remaining unchanged.



46%



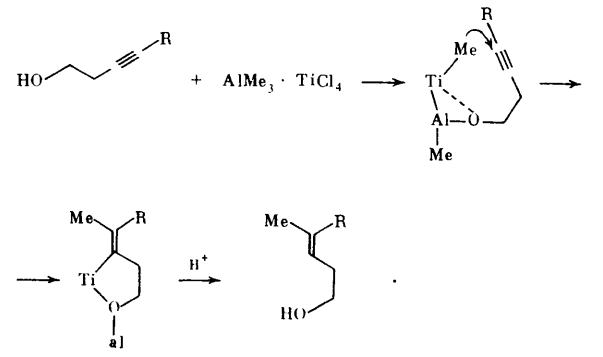
50–90%

n = 2–4.

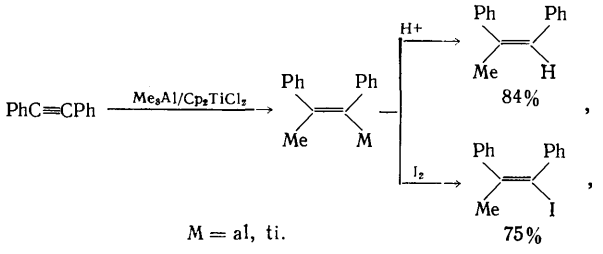
In this case Cp_2TiCl_2 has proved to be the best catalyst on conducting the reaction at 0 °C in methylene chloride during 4–6 h.

Evidently, reaction takes place via carbotitanation followed by transalkylation, although in isolated cases[66] it can be achieved easily in the presence of a catalytic amount (*ca.* 10 mol%) of the titanium reagent. However, as a rule, in order to obtain suitable yields, an equimolar amount of $TiCl_4$ or Cp_2TiCl_2 (relative to the starting alkyne) and twice the amount of OAC is required. According to certain authors,[67] the effective catalysts are four-valent titanium compounds which require activation by reduction to the three-valent state.

The regio- and stereo-selectivity of the reaction is determined by intramolecular formation of cyclic alkynyloxymetallic intermediates which are not disposed to β-hydride elimination or any other side reaction[62].

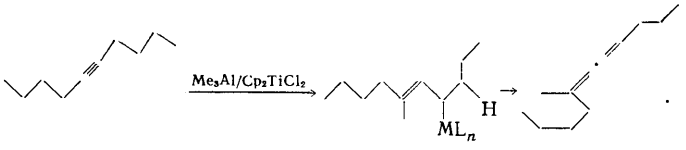


On the other hand, carboalumination of mono- and di-substituted alkynes which do not possess a hydroxyl group proceeds, as a rule, with low selectivity. Diphenylacetylene is an exception since it is readily carboaluminated under mild conditions with Me_3Al/Cp_2TiCl_2. The obtained OAC is converted on hydrolysis to (*Z*)-1,2-diphenylpropene (84%), while treatment with iodine affords 1-iodo-1,2-diphenylpropene (75%).[68]



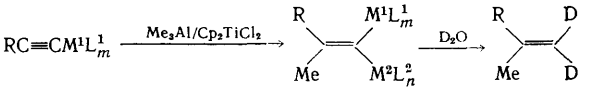
M = al, ti.

At the same time, reaction of dialkyl-substituted alkynes, e.g. 5-decyne, affords predominantly allenes:[68]



The yield of the products derived by carbometallation of monoalkyl-substituted acetylenes does not exceed 30%; unidentified oligomeric products are formed in the main.

For acetylenes functionalized at one of the unsaturated C-atoms by heteroatomic substituents (ZnCl, BR'_2, AlR'_2), the most selective system for carbometallation is Me_3Al/Cp_2TiCl_2.

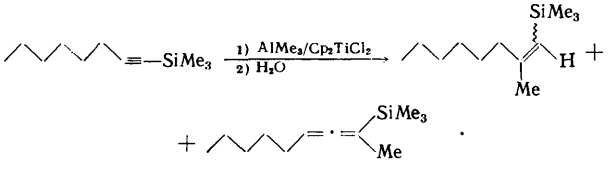


$M^1L^1_m$ = ZnCl, BR'_2, AlR'_2;

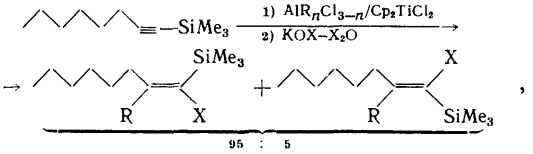
$M^2L^2_n$ = Al- and (or) Ti-containing group.

The heterobimetallic intermediates thus formed are converted on deuterolysis to 1,1-dideuterio-2-methylalkenes in 75–85% yield.[12]

In the case of carbometallation of 1-trimethylsilyl-1-alkynes, the yield and composition of the product is largely dependent on the reaction conditions and on the subsequent treatment of the intermediate alkenyl complexes. Thus, a mixture of vinyl- and allenyl-silanes was obtained in approximately 80% yield by carbometallation of 1-trimethylsilyl-1-octyne with trimethylaluminium.



Higher selectivity can be achieved by using halogen-containing alanes. In view of the marked increase in rate of the key step, the formation of side-products is kept to a minimum.[69]

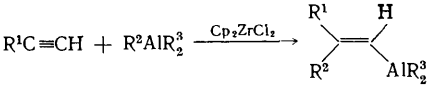


R = Me, Et; X = H, D.

The decomposition of the carbometallation product with aqueous KOH (or KOD in D_2O) is a critical stage which determines the reproducibility of the results; if an equimolar amount of triethylamine or another Lewis base is added before decomposition, then non-deuteriated isomeric vinylsilanes are formed, the *trans*-isomer predominating.[70] This effect is explained by the destabilising effect of the Lewis base on the intermediate alkenylaluminium complexes, which facilitates their protonolysis by the reaction medium.[71,72]

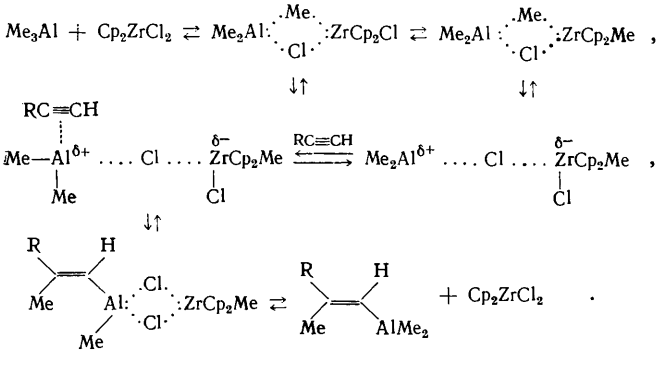
The problems normally associated with catalytic carboalumination of acetylenes have been overcome most effectively by using zirconium-containing catalysts. Discovered in 1978 by Negishi and Van Horn[69], the zirconium-mediated route has been studied in detail and found a place in synthetic organic chemistry for selective carboalumination of acetylenes; it is especially useful for the selective formation of isoprenoid residues, which are constituents of a large number of natural products. Because various aspects of this reaction have been discussed repeatedly in previous reviews,[12,72–77] only the fundamental characteristics of the reaction will be briefly touched on here.

As a rule the interaction of mono- or di-substituted acetylenes with alkylalanes affords the corresponding *cis*-adducts (*ca.* 98% stereochemical purity) in approaching quantitative yields.

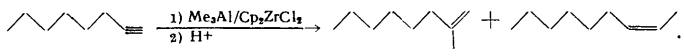


Reaction with trimethylalane is the most selective and that most often used; normally it is carried out in the presence of a catalytic amount (10 mol%) of Cp_2ZrCl_2. However, in certain cases, an equimolar amount of Cp_2ZrCl_2 and Me_3Al can be used to maximise the yield of desired product.

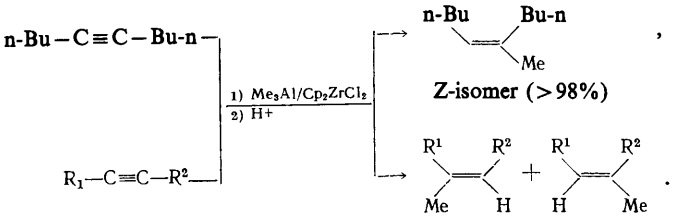
The mechanism of the reaction still requires clarification; however, current data would suggest that, in contrast with the corresponding titanium-catalysed process, it involves a direct interaction of the aluminium–carbon bond with the acetylene group.



Reaction of mono-substituted acetylenes with Me_3Al is not only stereoselective, but also regioselective.[79,80] Thus, 1-octyne, after appropriate treatment and hydrolysis, was converted into a 95:2 mixture of 2-methyl-1-octene and 2-nonene in a total yield of 97%:

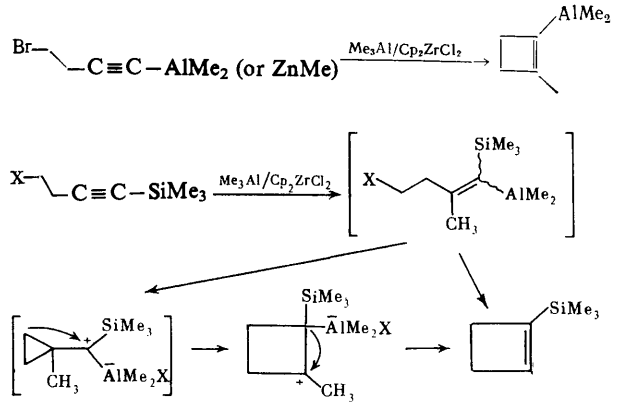


Symmetrically di-substituted acetylenes react with Me_3Al with the same stereoselectivity;[73] however for unsymmetrical substrates regioselectivity depends on the nature of the substituents.[12,78]

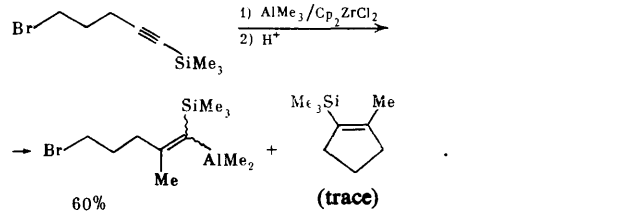


The overall yield is 89%. As well as alkyl groups, the alkyne component can contain such substituents as alkenyl, aryl, halogens, OH, OR', SPh, and $OSiR'_3$; alkadiynes are also reactive, but only one of the two multiple bonds is affected, even in the presence of an excess of $AlMe_3$.[81,82]

ω-Halogen-substituted acetylenes with trimethylsilyl, dialkylaluminium, or alkylzinc groups on the terminal carbon of the unsaturation are exceptions to the rule; here, functionalised cyclobutenes are formed instead of the expected adducts.[83,84]



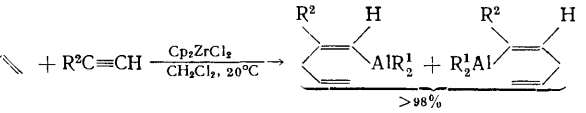
According to one report,[85] a π-type cyclisation is operative, in which the alkenyl fragment plays the role of nucleophile. The primary role of the σ-donor groups ($SiMe_3$, $AlMe_2$, ZnR) is to increase the nucleophilicity of the alkene. 5-Bromo-1-trimethylsilylalkynes are the least disposed to cyclisation, the principal products of reaction being acyclic.[85]



Unfortunately, the high (not less than 95%) regioselectivity associated with 'methylalumination' of terminal acetylenes falls to 75–85% on replacing the Me_3Al by other trialkylalanes.[12]

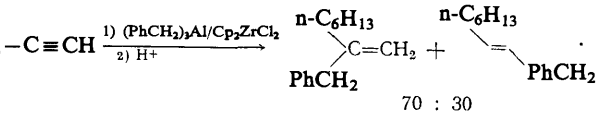
In addition to this, catalytic hydroalumination is a serious complication with those alkylalanes which are inclined to undergo β-hydride elimination. However, such hydroalumination can be successfully suppressed by using such reagent/catalyst combinations as $R_2AlCl-Cp_2ZrCl_2$ and $R_3Al-Cp_2Zr(R')Cl$.[12,86]

On account of the reduced regioselectivity, carboalumination with $AlEt_3$, $AlPr_3$ and other simple trialkylalanes has little synthetic value. The reactions of allyl- and benzyl-alanes with mono- and di-substituted acetylenes are no exception to this generalisation.[87,88]



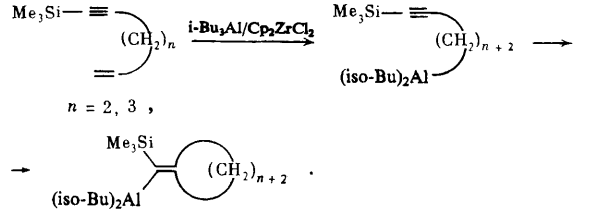
Here, stereoselectivity is almost 100%, but high regioselectivity is found only in the case of phenyl-substituted acetylenes. Reaction is impeded if a Me_3Si group is situated on the triple bond and in the presence of more than one equivalent of an ethereal solvent. Dimethyl- and diisobutyl-allylalanes have both been used as allylating agents; however in the latter case simultaneous hydroalumination may take place with the participation of the isobutyl group. Allylaluminium sesquibromide was shown to be inactive.

By comparison with allylalanes, benzylalanes are less active; reaction of $(PhCH_2)_3Al$ with 1-octyne takes place only at elevated temperatures (from 60 °C), affording a mixture of regioisomers in 90% total yield after 48 h.

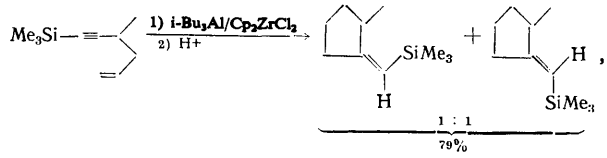


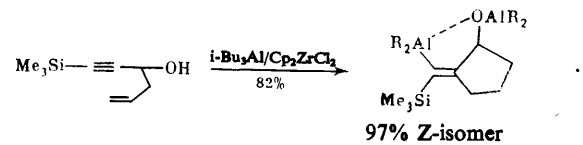
By replacing $(PhCH_2)_3Al$ with $(PhCH_2)_2AlMe$, products are formed via both benzyl- and methyl-alumination in approximately equal proportion, but $i\text{-}Bu_2AlCH_2Ph$ reacts only by cleavage of the isobutyl group.

Finally, as one further example of zirconium-catalysed carboalumination, the intramolecular variant leads to the formation of exocyclic alkenylalanes. In this case, the carbometallating agent is regenerated *in situ* as a result of interaction of $i\text{-}Bu_3Al$ with the double bond of the starting enyne.[88,89]



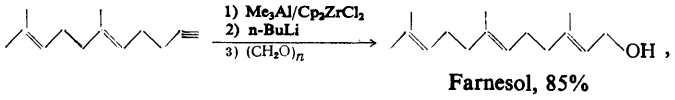
In almost all examples, reaction is non-stereoselective.



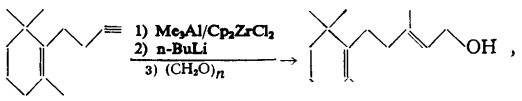


In all of the above-mentioned examples of Cp_2ZrCl_2-catalysed carbometallation of terminal acetylenes with Me_3Al, the most useful synthetic aspect is the generation of key intermediates with high stereo- and regio-selectivity, as well as the high reactivity of the formed vinylalanes. The latter can be readily converted into other metallo-derivatives, e. g. boron, zirconium and mercury analogues, as well as into halogeno- or deuterium-containing hydrocarbons and compounds containing a variety of functional groups.[76]

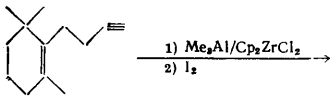
The reaction has been used in the synthesis of an entire series of natural and biologically active compounds containing an isoprenoid residue, e. g. farnesol, geraniol. monocyclofarnesol, ocimene, α-farnesene (see p. 1167), vitamin A, mokupalide, brassinolide, dendrolasin, milbemycin, verrucarin, zoapatanol and others.[75,76,90–102]

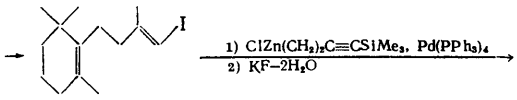


Farnesol, 85%

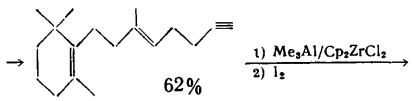


Monocyclofarnesol, 71%

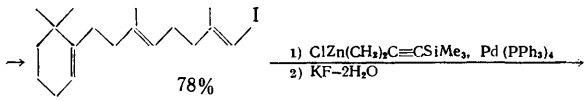




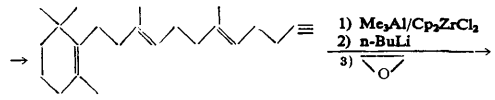
65%



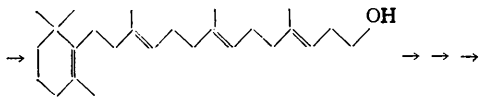
62%



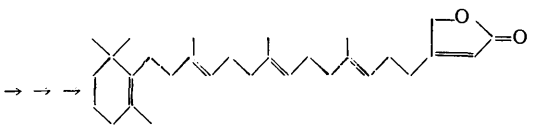
78%



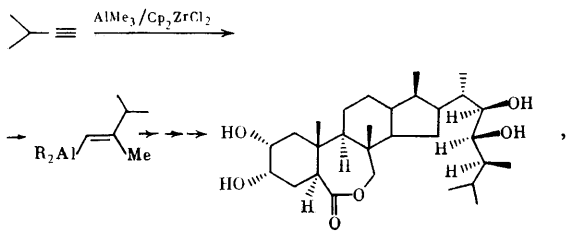
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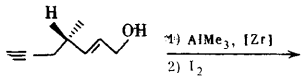
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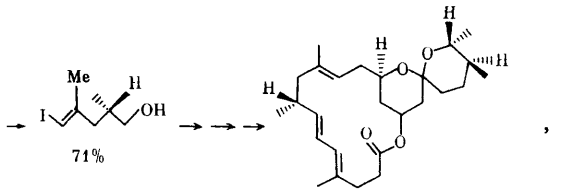


Mokupalide 50%

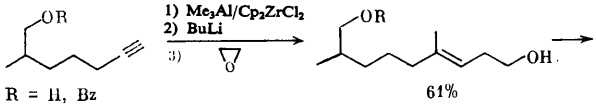


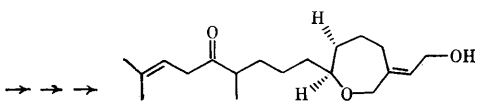
Brassinolide





Milbemycin



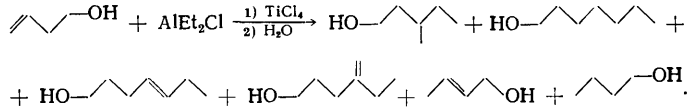


Zoapatanol

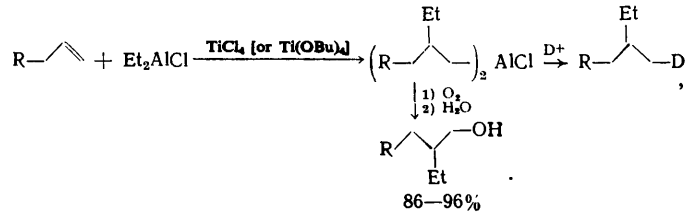
No doubt the more widespread application if this reaction has been restricted by the difficulties associated with handling concentrated solutions of trimethylaluminium.

2. Carboalumination of α-olefins

A significantly fewer number of publications have been devoted to the catalytic carboalumination of olefins. Thus, in contrast with homopropargyl alcohols,[63,67] homoallylic analogues are carboaluminated with very low selectivity on reaction with trialkylalanes or dialkylaluminium halides in the presence of titanium reagents ($TiCl_4$, $TiCl_2(acac)_2$, Cp_2TiCl_2).[63,67,103–105] Because of associated hydrometallation, hydrogenation, isomerisation and β-hydride elimination (in varying proportions), the yield of the regioisomeric mixture of OACs does not exceed 10–30%.

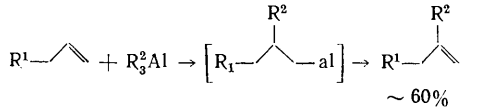


There are references to the selective carboalumination of α-olefins (C_6 to C_{12}) with diethylaluminium chloride in the presence of small amounts (0.5 to 3 mol%) of $TiCl_4$ or $Ti(OBu)_4$ at 20 °C in toluene over the course of 3 h.[106,107]

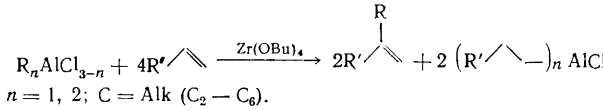


86–96%

Carboalumination of α-olefins with trialkylalanes in the presence of a stoichiometric amount of Cp_2TiCl_2 leads predominantly to the formation of products derived by β-hydride elimination, in addition to high molecular weight oligomers.[108]

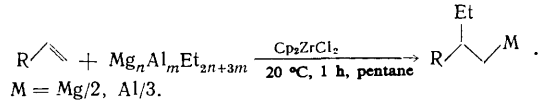


In the presence of a catalytic amount of $Zr(OBu)_4$, the analogous reaction with halogenalanes proceeds far more selectively, affording, in varying yield, products derived by β-alkylation of the starting olefins, in addition to the corresponding higher di-*n*-alkylaluminium halides.[51,109–112]

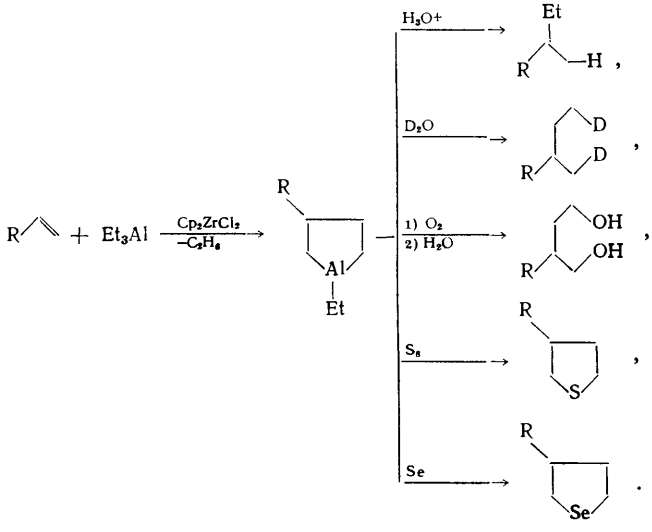


It is not possible to interrupt the process at the stage of carbometallation, even by varying reaction conditions and the proportion of starting materials; evidently, all stages proceed in one and the same catalytic matrix. The best yields were obtained by using dialkylaluminium halides, the activity of which was somewhat reduced with increase in the size of the hydrocarbon radical.[109] α-Olefins have been used as the unsaturated substrate; these may contain aryl substituents (but not OR or OH), as well as disubstituted double bonds. The latter do not react with alkylaluminium halides, but may undergo isomerisation.

It has been shown that, contrary to earlier reports,[51,97,111] triethylaluminium selectively carboaluminates α-olefins under the action of zirconium-containing catalysts, but only as complexes with Et_2Mg[106]

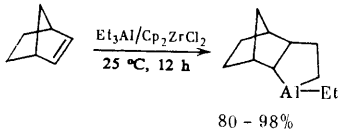


By interaction of an excess of Et_3Al with olefins in the presence of a catalytic amount of Cp_2ZrCl_2, β-substituted aluminacyclopentanes are formed along with evolved ethane; carboalumination does not take place under these conditions:[112,113]

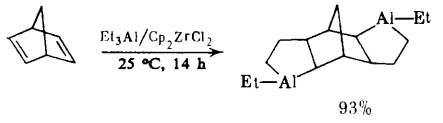


The described reaction is the first example of a catalytic cyclometallation. Although analogous catalytic reactions of organomagnesium and -lithium compounds are known,[116–118] this reaction type is normally found only in transition metal chemistry (as the non-catalytic variant).[114,115] The formation of intermediate zirconacyclopentane complexes has been proposed as the key step in the above reaction.[119–120]

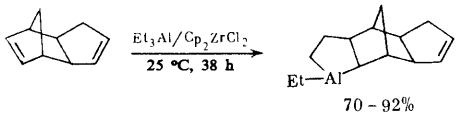
Not only α-olefins (including those with aryl and alkenyl substituents[121]) but also norbornene and some of its derivatives[122–124] may participate in the reaction with Et_3Al.



(Ref.122)



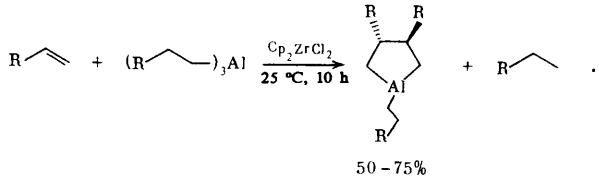
(Ref.123)



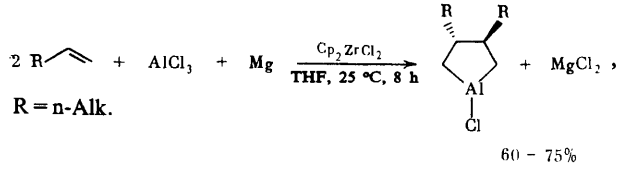
(Ref.124)

It is interesting to note that, on cyclometallation of norbornadiene, there is no formation of nortricyclene derivatives as observed with catalytic carbomagnesation[125] and hydroalumination.[46]

On replacement of $AlEt_3$ by higher trialkylalanes, their activity in the cyclometallation of α-olefins decreases.[126]



1-Chloroaluminacyclopentanes are formed by interaction of 2 equivalents of the α-olefin with $AlCl_3$ in the presence of Mg-powder and a catalytic amount of Cp_2ZrCl_2:



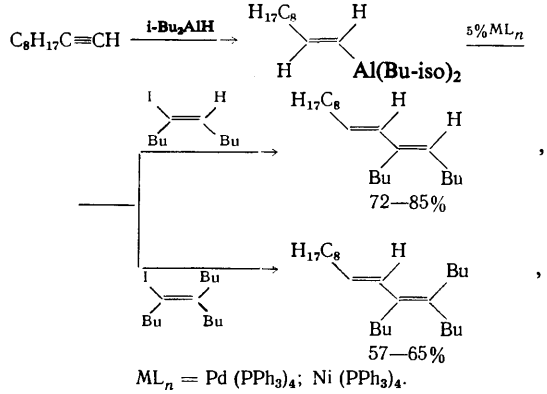
With the discovery of catalytic cyclometallation, there are wide possibilities for pursuing studies in a new field of organometallic chemistry: the chemistry of metallocycles of non-transition metals, the properties of which have, up to this time, remained almost unexplored. Thus, the obtained aluminacyclopentanes are extremely interesting synthetically, their reactivity differing from that of acyclic alkylalanes. In particular, they have proved to be suitable synthons

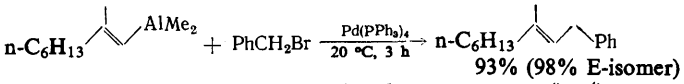
for the preparation of a variety of heterocyclic compounds,[127–131] and have found a use in natural product synthesis.[132–135] At the present time, much research is being performed on the reactions of alumina- and magnesia-cyclopentanes; some of their catalytic conversions will be examined below.

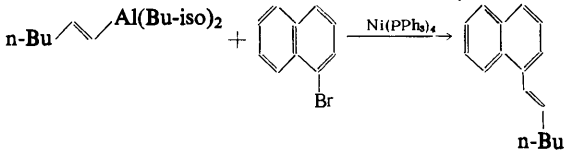
IV. Catalytic cross-coupling with organoaluminium compounds

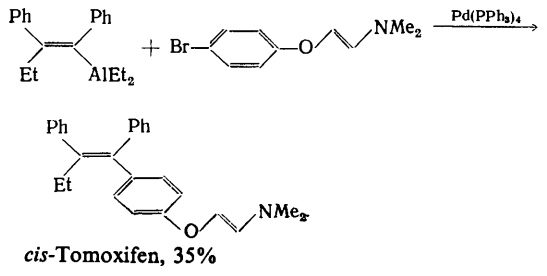
Discovered less than twenty years ago, catalytic cross-coupling is now one of the most generally applicable and far-reaching methods of forming the carbon–carbon bond from organometallic compounds. Among organoaluminium compounds which participate in cross-coupling, alkyl- and vinyl-alanes are most frequently used. This is, in part, because of their availability (via the above-described hydro- and carbo-metallation) and, in part, because of their ability to react selectively with a variety of electrophiles in the presence of a catalytic amount of transition metal complexes, notably Ni, Pd or Cu complexes.

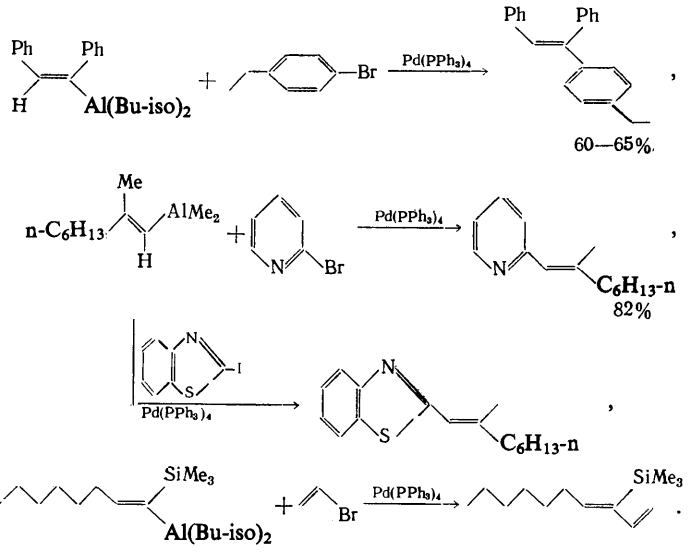
Negishi et al.[136,137] have developed an excellent method of preparing conjugated dienes and arylalkenes of defined configuration via Ni- or Pd-catalysed coupling of vinylalanes with alkenyl, aryl or benzyl halides. The method has been applied to the synthesis of a number of biologically active compounds or synthons for their preparation.[138–142]



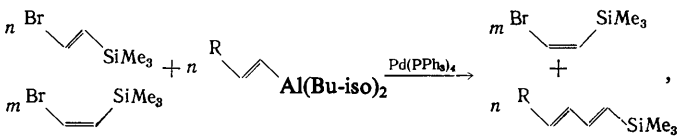




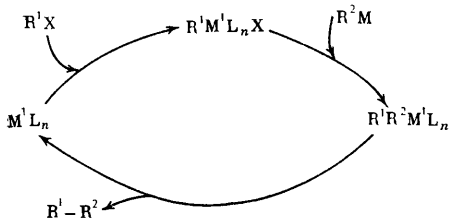




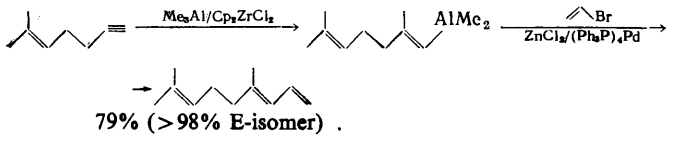
In all variants of the above cross-coupling, almost 100% stereospecificity results by using Pd-catalysts; however, there is some loss of stereoselectivity in the synthesis of conjugated dienes with Ni-complexes. Cross-coupling of (*E*)-1-alkenylalanes with a stereoisomeric mixture of (2-bromovinyl)trimethylsilanes proceeds stereoselectively in the presence of $Pd(PPh_3)_4$ (in THF–hexane at 40 °C for 16 h) with the formation of 4-alkyl-substituted (1*E*, 3*E*)-1-tri-methylsilyl-1,3-dienes, the stereo-purity of which exceeds 99%.[143]



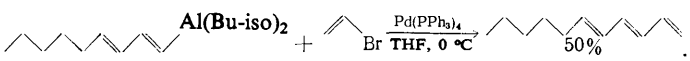
According to a specifically mechanistic study, it was established that cross-coupling proceeds through an initial oxidative addition of a Pd(0)-complex, followed by a rate-determining transmetallation with participation of an organopalladium(II) complex, and rapid decomposition of the diorganopalladium complex formed to give the cross-coupling product.[144]



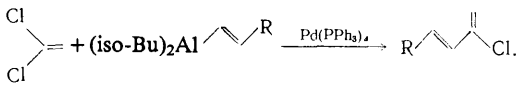
For cross-coupling of sterically hindered vinylalanes (notably those obtained by Zr-catalysed carboalumination) with vinyl halides it is necessary to use the bimetallic catalyst, $Pd(PPh_3)_4/ZnCl_2$.[145]



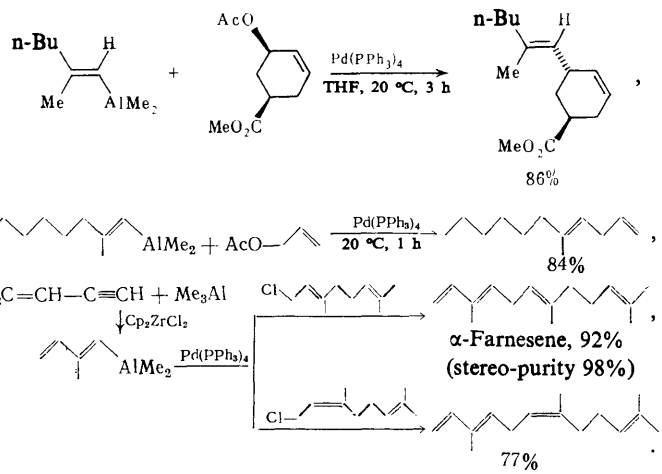
Without $ZnCl_2$ the yield remains below 1%. Dienylalanes may also undergo cross-coupling, although the products are obtained in high yield without $ZnCl_2$.[146]



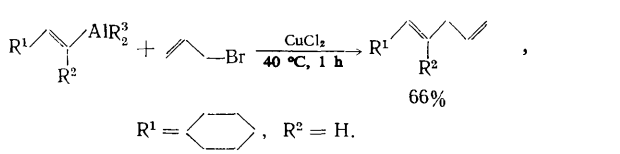
In the case of 1,1-dihalogenoalkenes, it is possible to replace selectively one of the chlorine atoms.[147]



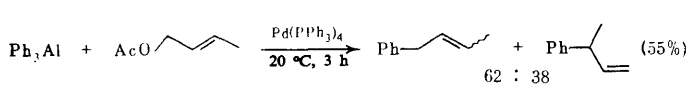
Allyl halides and acetate also afford excellent yields of cross-coupling products with vinylalanes in the presence of Pd-complexes.[148–149]



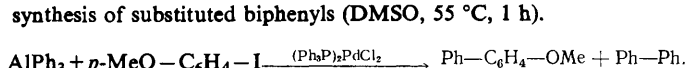
The reaction of allyl halides with vinylalanes is also catalysed by copper salts.[150]



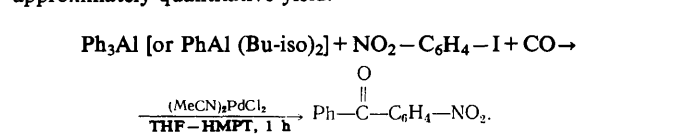
Examples of Pd-catalysed cross-coupling of arylalanes with allylic and aryl electrophiles are known:[151]



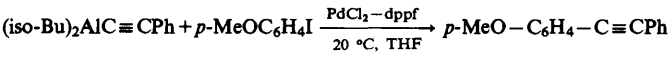
The coupling of arylalanes with aryl halides proceeds more selectively.[152,153] The reaction is of preparative value for the synthesis of substituted biphenyls (DMSO, 55 °C, 1 h).



By conducting this reaction in the presence of carbon monoxide, substituted aromatic ketones were obtained, sometimes in approximately quantitative yield:[154]

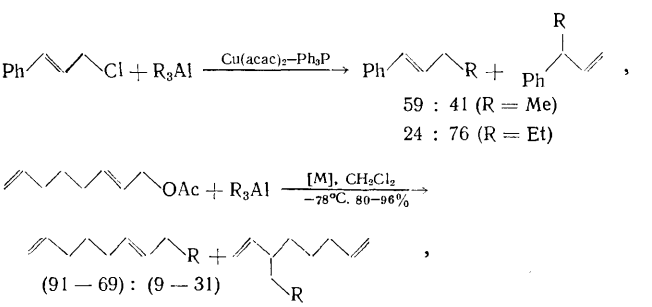


Cross-coupling of alkynylalanes normally proceeds non-selectively due to the formation of a large amount of product derived by homo-coupling.

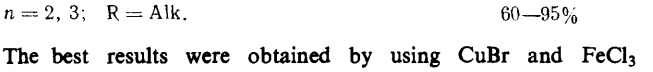


The maximum yield (42%) was achieved by using a catalyst containing diphenylphosphinoferrocene (dppf).[153]

The reaction of alkylalanes and lithium tetraalkylaluminates with allylic electrophiles can, in principle, be conducted in the absence of catalyst; however, the selectivity and yield of coupling products are not high. Reaction is favoured by using copper-containing catalysts, and in a number of cases there is an effect on selectivity.[155–159]

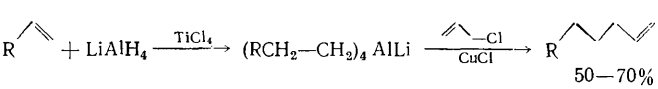


R = n-C_6H_{13}, *i*-Bu, Et; [M] = CuBr, CuCl, $FeCl_3$.

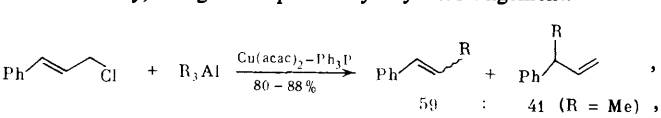


The best results were obtained by using CuBr and $FeCl_3$ as catalysts; with Pd-containing catalysts the selectivity is worse, although they have been successfully used in the cross-coupling of alkylalanes with certain halogenonucleosides (8-bromoadenosine and 5-bromouridine).[160]

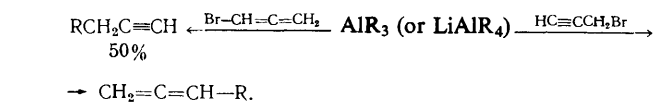
Lithium tetraalkylaluminates react in a similar manner with allyl halides in the presence of mono- and di-valent copper salts [CuCl, CuBr, CuI, CuCN, $CuCl_2$ and $Cu(OAc)_2$]. Contrasting with trialkylalanes, which participate by donating only one alkyl group, tetralkylaluminates transfer all four ligands.[34]



In the case of substituted allyl halides, reaction takes place as a rule non-selectively, being accompanied by allyl rearrangement:[161,162]

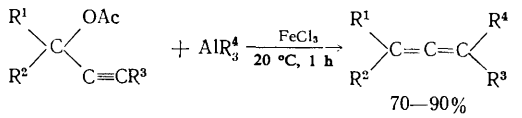


At the same time, products of rearrangement predominate on reaction of propargyl and allenyl halides with alkylalanes and alkylaluminates in the presence of CuCl at 0 °C during 5 h; the result is an original preparative route to primary allenes and acetylenes.[163–166]



The reaction of substituted propargyl acetates with trialkylalanes and

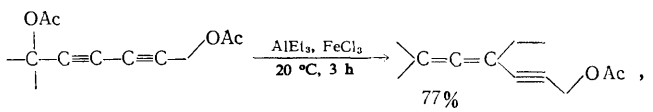
alkenyldialkylalanes proceeds readily in the presence of $FeCl_3$ (in this case being a more active catalyst than Pd or Cu salts), thereby providing a suitable method for preparing substituted allenes, including functionalised vinylallenes, diallenes and allenynes. A variety of different OACs may participate in the reaction. The obtained vinylallenes are of practical value as synthons for the preparation of a number of natural products with a cyclopentanone residue.[167–171]

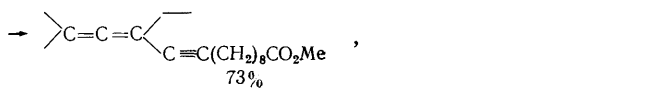


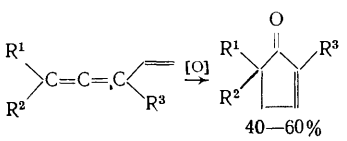
70—90%

R^1, R^2 = Me, Et, $CH{=}CH_2$; R^3 = H, $CH{=}CH_2$;

R^4 = Et, Me, *i*-Bu, n-C_6H_{13};



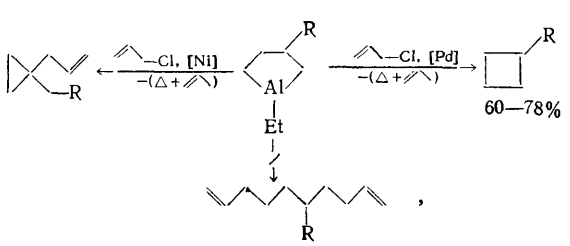




R^1, R^2, R^3 = H, Alk.

It is worth noting that reaction takes place preferably at the electrophilic centre of the propargyl group even in the presence of an allyl group (when R′ = $-CH{=}CH_2$).

Allyl halides react in an unusual manner with aluminacyclopentanes, the formation of which has been mentioned in the previous section under cyclometallation.[12,113] Thus, interaction of substituted aluminacyclopentanes with allyl chloride in the presence of palladium complexes affords mono-substituted cyclobutanes,[172] while allylcyclopropanes are obtained in the presence of nickel catalysts.[173]



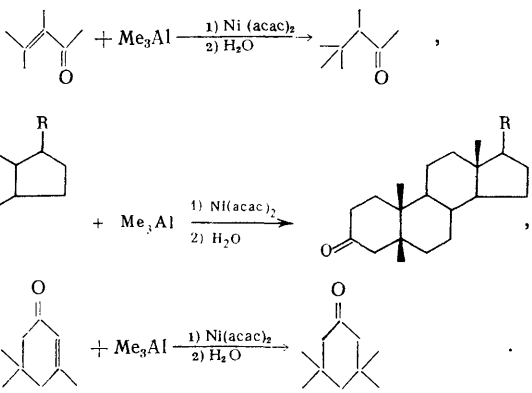
R = Alk.

Reaction is accompanied by the evolution of a mixture of propylene and cyclopropane.

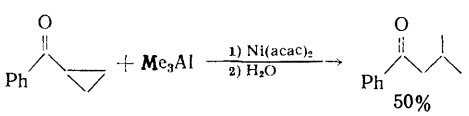
V. Catalytic reactions of organoaluminium compounds with carbonyl-containing compounds

1. Conjugate addition

It is known that reduction and alkylation of enones can proceed by both 1,2- and 1,4-addition. Both types of reaction are known with organoaluminium reagents. Selective 1,4-addition of Me_3Al to enones can be achieved in the presence of $Ni(acac)_2$.[174–176]

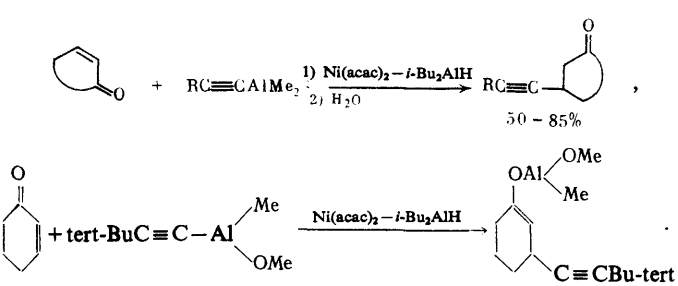


Cyclopropyl ketones react in a similar manner under these conditions:[175]

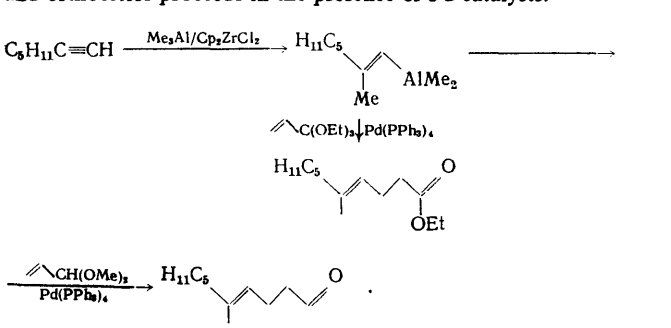


All such additions are normally complicated by the formation of high molecular-weight products derived by aldol condensation.

Dialkylalkynylalanes react with α,β-enones by donating only an alkyl group.[177,178] In order to obtain high yields of the alkynyl adduct, the catalyst must be preliminarily reduced by *i*-Bu_2AlH:

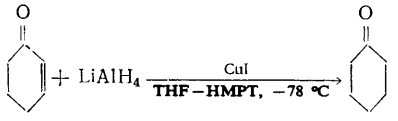


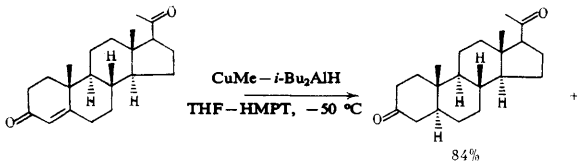
The analogous reaction of vinylalanes with α,β-unsaturated acetals and orthoesters proceeds in the presence of Pd-catalysts.[174]

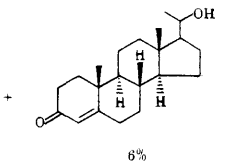


2. Conjugate reduction of enones

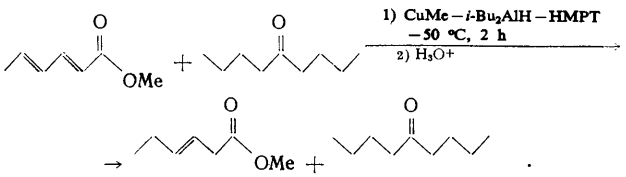
Conjugate reduction of α,β-unsaturated carbonyl compounds with *i*-Bu_2AlH [179] or $LiAlH_4$ [180] is catalysed by Cu(I) compounds, and proceeds in the presence of hexamethylphosphoramide (HMPT):







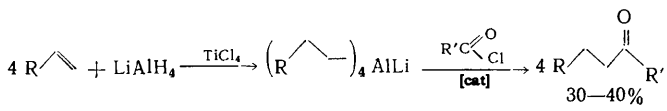
In the case of dienones, selective 1,6-reduction takes place even in the presence of an equivalent amount of saturated carbonyl compound:[180]



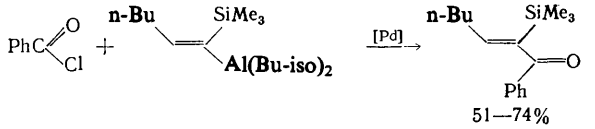
Triisobutylaluminium reacts with α,β-unsaturated ketones in the same way, but in the presence of nickel complexes.[181]

3. Synthesis of ketones

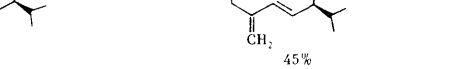
The interaction of OACs with acyl chlorides in the presence of transition metal salts may be applied as an effective method of preparing ketones:[35,182,183]



Palladium complexes [$Pd(PPh_3)_4$ and $Pd(OAc)_2.2PPh_3$] are the best catalysts for the selective synthesis of ketones from OACs containing alkenyl or alkynyl groups, whereas Ru-, Rh- and Ni-complexes were ineffective.[183]

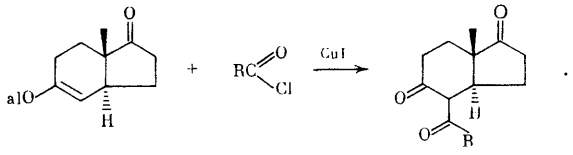


Trialkylalanes afford a better yield of ketones than tetraalkylaluminates,[182] and react not only with acyl chlorides but also with thiolocarboxylic acid esters:



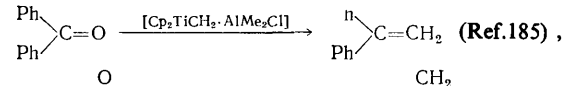
X = Cl, SPh; R^1 = Ph, $CH_2=CH-(CH_2)_8-$; R^2 = Me, Et, *i*-Bu.

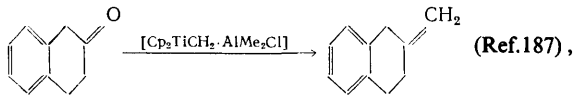
In addition, copper(I) salts catalyse the formation of 1,3-diketones from acyl chlorides and aluminium enolates:[184]

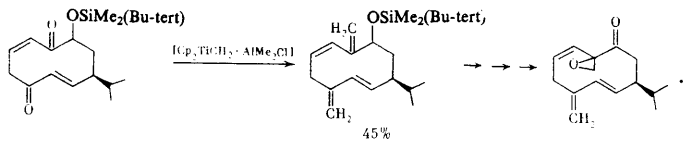


4. Methylenation of carbonyl compounds

Tebbe's reagent ($Cp_2TiCH_2.AlMe_2Cl$), prepared *in situ* by treatment of Cp_2TiCl_2 with Me_3Al,[185,186] has proved to be useful for the methylenation of a variety of carbonyl compounds. It can serve as an alternative to the traditional Wittig reagent, notably for the methylenation of readily enolisable ketones which are unstable under the strongly basic conditions of the Wittig synthesis.



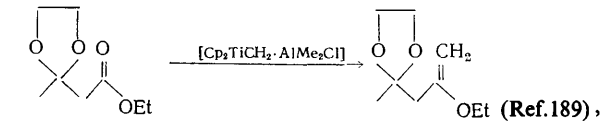


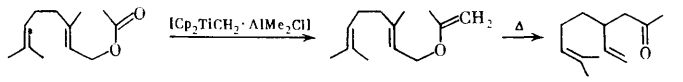


(Ref.188)

Esters and lactones are simply converted to the corresponding enolethers which may then react further:[189,190]





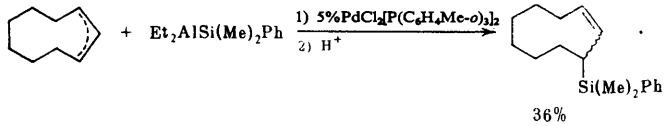


(Ref.190).

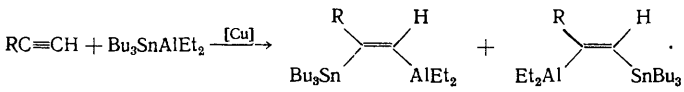
VI. Catalytic reactions across the aluminium-heteroatom bond

This section will be devoted to some interesting reactions related to carbometallation and cross-coupling which were discussed earlier; however, we shall be considering here reaction across the aluminium-heteroatom bond, rather than the aluminium-carbon bond (even in cases where the OAC contains both aluminium-heteroatom and aluminium-carbon bonds). In this way, a variety of hetero-functions

can be introduced into an organic compound. Thus, silylalumination of the allene group of 1,2-cyclononadiene with dimethyl(phenyl)silyldiethylalane in the presence of a Pd-catalyst affords a 3-dimethyl(phenyl)silyl-1-cyclononene:[191]

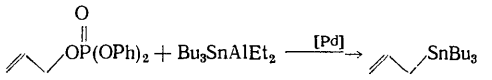


By interaction of mono-substituted acetylenes with dialkyl(stannyl)-alanes in the presence of Cu(I) salts (CuCN, CuI) or Pd(O)-complexes, stannylalumination of the triple bond takes place rather than carboalumination:[192–195]

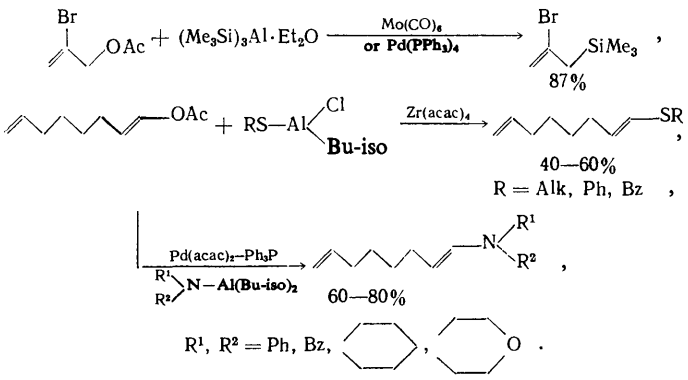


Reaction is noteworthy for its high regio- and stereo-selectivity (80–92%). Contrasting with carbometallation, stannylalumination can be performed on acetylenes which possess tetrahydro-2-pyranyloxy-, hydroxy-, acetoxy-, and benzyloxy-groups.

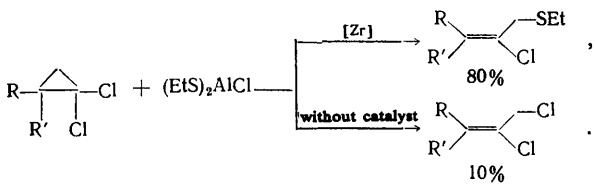
By interaction of (tributylstannyl)diethylalane with allyl phosphates, cross-coupling takes place with the formation of allylstannanes:[196]



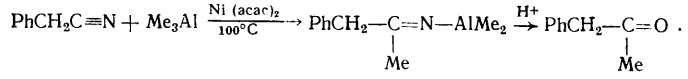
Similar reactions can also be achieved by fission of Al–Si [197], Al–N and Al–S bonds.[198,199]



Finally, by interaction of *gem*-dichlorocyclopropanes with bis(ethylthio)aluminium chloride in the presence of Zr-catalysts, a high yield of the corresponding allyl thioethers was obtained, i.e. the chlorocyclopropane here performs the function of an allyl halide equivalent.[200]



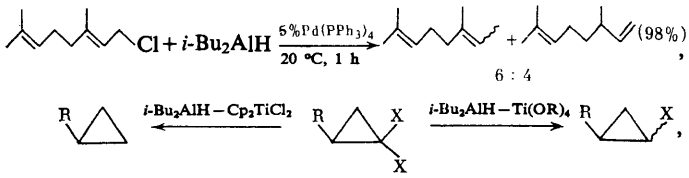
Addition of Me_3Al to the nitrile bond of alkyl, aryl and benzyl cyanides is analogous to carboalumination of acetylenes.

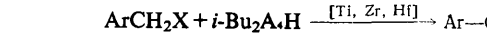


Reaction is more selective and milder in the presence of Ni-complexes[201] than without catalyst.

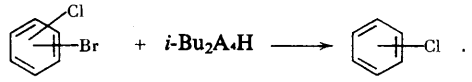
VII. Other catalytic reactions involving organoaluminium compounds

In the presence of palladium complexes,[202] as well as those of Ti, Zr and Hf,[202–207] *i*-Bu_2AlH effectively dehalogenates various types of halogenated hydrocarbon under mild conditions. These include allyl,[202] alkyl,[204] aryl[204] and cyclopropyl halides:[203–207]

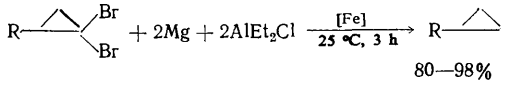




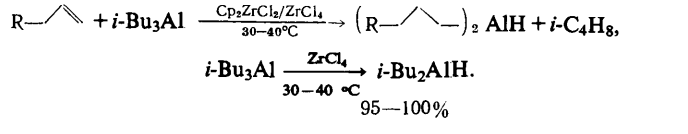
In the case of aryl bromides containing aromatic chlorine, it is possible to replace the bromine with retention of the C–Cl bond.[204]



Complete dehalogenation of dibromocyclopropanes can be achieved with a mixture of Et_2AlCl and powdered magnesium in the presence of $FeCl_3$ as catalyst.[208]



The synthesis of *i*-Bu_2AlH and certain higher dialkylaluminium hydrides was carried out under mild conditions with the aid of zirconium catalysts:[209,210]



Higher alkylaluminium chlorides have been obtained by catalytic telomerisation of ethylene with diethylaluminium or sesquiethylaluminium chloride, also in the presence of zirconium catalysts.[211]

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Key steps in the cross-coupling of organometallic compounds with organic halides, catalysed by nickel and palladium compounds

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ABSTRACT. The mechanism of cross-coupling of organometallic compounds with organic halides, catalysed by nickel and palladium complexes, has been examined. The key steps are discussed: oxidative addition, transmetallation, and reductive elimination. There is an analysis of the problems associated with the choice of the most effective ligands for the nickel and palladium complexes.

The bibliography contains 100 references.

Contents

I.	Introduction	1174
II.	Oxidative addition	1175
III.	Transmetallation	1178
IV.	Reductive elimination	1179
V.	The influence of the ligand environment in the transition metal complex on the efficiency of cross-coupling	1182

I. Introduction

A major problem in organic chemistry is the development of highly selective reactions in which carbon–carbon bond formation takes place. One such reaction is cross-coupling wherein organometallic compounds (notably of lithium and magnesium) interact with organic halides.

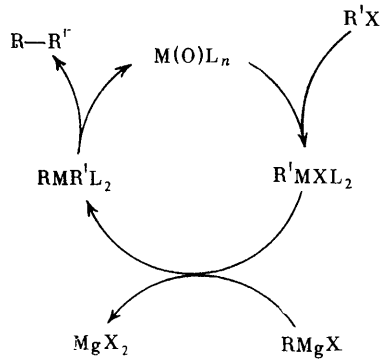
$$RM + R'X \rightarrow R{-}R' + MX. \quad (1)$$

However, cross-coupling has found a limited application in organic synthesis for two reasons: firstly, on account of concurrent elimination and exchange which leads to decrease in selectivity; and, secondly, on account of the inertness of organic halides possessing a halogen on an sp^2 atom. These limitations and associated practical difficulties can be overcome to a large extent by using organocopper compounds (in particular organocuprates) in place of organo-lithium or -magnesium reagents.[1,2] However, many problems remain unsolved. For example, cross-coupling with the formation of a carbon–carbon bond between sp^2 atoms proceeds with low selectivity; organic halides with reactive functional groups cannot always be used; and reactions with copper acetylides require fairly harsh conditions.

A new impulse to cross-coupling was given in the early 1970s when Kumada and Corrius et al.[3,4] demonstrated independently that cross-coupling of Grignard and organolithium compounds with alkenyl and aryl halides proceeds readily in the presence of nickel complexes. In 1975, it was shown[5] that the palladium complex, $Pd(PPh_3)_4$, is an effective catalyst for the reaction. Cross-coupling with more active organometallic compounds of (zinc,[6] aluminium,[7] zirconium,[8], boron,[9] tin [10] and mercury [11]) has significantly broadened the scope of the method, permitting the synthesis of various types of organic compound containing almost any functional group.

Since palladium- and nickel-catalysed cross-coupling proceeds under mild conditions in high yield and with high selectivity, the method has been widely applied in organic synthesis. Synthetic aspects of cross-coupling have been examined in earlier reviews.[12–17] This review is devoted to a detailed study of the mechanism of cross-coupling; a comparison is made of various organometallic compounds, RM in Eqn. (1), by considering the nature of the organic residues, R and R', and the metal, M; and the effect of the particular nickel of palladium catalyst has been studied.

For nickel- and palladium catalysed cross-coupling of Grignard reagents with organic halides, it is generally accepted that the mechanism of the reaction involves an initial oxidative addition of R'X to the zero-valent metal complex, M(0) followed by transmetallation with formation of a complex, $RMR'L_2$, having two σ-bonded organic residues; reductive elimination of R–R' completes the cycle with regeneration of M(0) [3,18] (scheme 2):



(2)

Nickel and palladium complexes are known to participate in the individual stages of this catalytic cycle. Thus, oxidative addition of aryl halides to PdL_4 leads to the formation of palladium σ-complexes, *trans*-$ArPdXL_2$.[19] By interaction of such complexes with RMgX, diorganopalladium complexes, *trans*-$ArPdRL_2$, are obtained. Some of these complexes have been isolated in pure form, e.g. where R = Me, Ph; Ar = *p*-FC_6H_4; L = PEt_3. In solution complexes $ArPdRL_2$ gradually cleave with the formation of cross-coupling product.[20] However, scheme (2) reflects only the most characteristic features of catalytic cross-coupling. There is no indication, for example, of the configuration of the mono- and di-organo-complexes, and no indication of the precise mechanism of the ligand exchange, etc. There is a detailed discussion below of

oxidative addition, reductive elimination, and transmetallation. Although cross-coupling is performed primarily in the presence of palladium and nickel catalysts, other transition metals will be considered with a view to elucidating general trends.

II. Oxidative addition

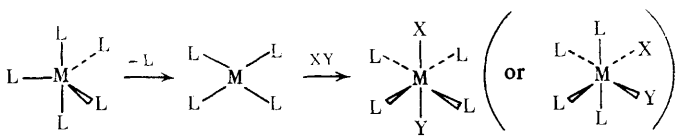
Oxidative addition is defined as the reaction of a transition metal complex with a substrate X–Y (H_2, O_2, RX, RH, etc.) wherein a covalent bond in the latter is cleaved with an associated one- or two-electron oxidation of the metal.[21]

$$X-Y+2M\rightarrow M-X+M-Y \text{ (or } X-M-M-Y) \quad (3)$$

$$X-Y+M\rightarrow X-M-Y \text{ (or } X-M^{+}Y^{-}) \quad (4)$$

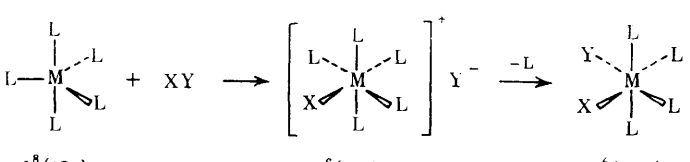
This reaction is characteristic of transition metal complexes in low oxidation states, especially complexes of Group VIII metals having a d^8- and d^{10}-electronic configuration. Oxidative addition is accompanied by a shift in the *d*-configuration from d^n to d^{n-1} or d^{n-2} with an increase in the coordination number. The reverse process, known as reductive elimination, is characterised by a decrease in the oxidation state of the transition metal. Clearly, it is because transition metals are able to exist in a number of oxidation states and are able to transfer easily from one oxidation state to another that they catalyse many reactions. On the contrary, oxidative addition and reductive elimination are quite uncharacteristic of non-transition metals. Thus, the latter do not catalyse cross-coupling. It should be pointed out that the term, oxidative addition, describes only the result of reacting X–Y with a transition metal complex, and is not a mechanistic definition.

In order to participate in oxidative addition, the transition metal complex may be either coordinatively saturated or unsaturated. The reactivity of coordinatively unsaturated complexes is, as a rule, significantly higher. There is an initial ligand dissociation on interaction of substrates, XY, with 5-coordinate 18-electron metal complexes with a d^8-configuration.



(5)

Coordinatively saturated d^8-complexes interact only with reagents having powerful oxidising properties. Reaction proceeds via intermediate formation of an octahedral cationic d^6-complex.

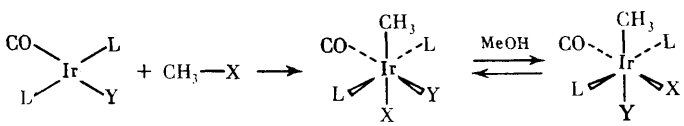


(6)

For substrates, XY, participating in oxidative addition one can designate three classes: class A are polar, electrophilic reagents; class B are reagents in which the bond between X and Y remains intact after oxidative addition; and class C are non-polar reagents.[21] Halogens (X_2), acids (HY), RSCl, RSO_2Cl, RX, RCOX, R_FI, RCN, $SnCl_4$, and HgX_2, for example, belong to class A; O_2, S_2, Se_2, *o*-quinones, RC≡CR, RN=NR, RCH=CHR, CS_2, CH_2O, cyclopropanes, $RCON_3$ and RN_3 are in class B; and H_2, R_3SiH, R_3GeH, R_3SnH, RSH, RCHO, ArH and RH are in class C. Of the multitude of oxidative oxidations,[21] we shall examine below only reactions involving organic halides (class A) in the presence of transition metal complexes.

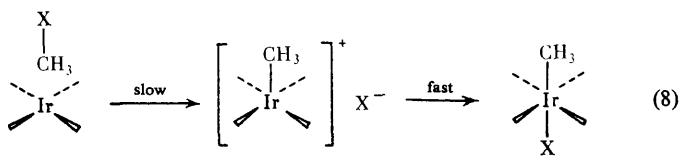
As low-valent transition metal complexes are basically nucleophilic, they readily react with alkylating agents. However, in contrast with familiar nucleophilic reagents, zero-valent metal complexes do interact with aryl and alkenyl halides. In mechanistic terms, reaction may involve an S_N2-process, a radical chain process, or a single-electron transfer (SET), depending on the formal charge on the metal complex, the nature of the metal, the ligand environment, the structure of the organic halide, and on the conditions under which oxidative addition is performed.

The oxidative addition of methyl halides to an iridium(I) complex is representative.



(7)

A kinetic study has shown that the reaction is of the second order (first order in each reactant).[22] The rate of the reaction increases with solvent polarity, being in the order: DMF > MeCN > THF > C_6H_5Cl > C_6H_6; and the large negative entropy of activation accords with an S_N2 mechanism for nucleophilic substitution of a carbon atom. It should be pointed out that it was not possible to intercept the 5-coordinate cationic iridium(III) intermediate (scheme 8) with an external nucleophile.[23]



(8)

A *trans*-methyliridium(III) complex is formed in non-polar solvents as a result of oxidative addition. In methanol the *trans*-complex isomerises to the thermodynamically more stable *cis*-complex.[24] A radical chain mechanism was excluded since the rate of oxidative addition is unaffected in the presence of radical traps.

The rate of reaction (7) increases with the basicity of the phosphine ligand L:

$$PEt_3 > PEt_2Ph > PEtPh_2 > P(p\text{-Tol})_3 > PPh_3.$$

However, in a number of cases, a steric effect can be the dominant factor.[25] For example, complexes where L = $PPhMe_2$ are more active than those where L = PEt_3. Evidently, this would also explain the higher rate of oxidative addition of CH_3X to the complex $FIrCOL_2$ than to $IIrCOL_2$.

Ethyl iodide is significantly less reactive than methyl iodide, and secondary alkyl halides in general do not participate in reaction (7) in the absence of a radical initiator. These results are also consistent with an S_N2 process.

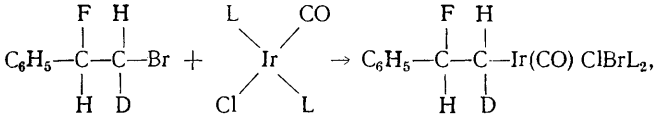
Secondary, and even primary, alkyl halides which are inactive in S_N2 reactions readily react with Ir(I) complexes by a radical chain

mechanism. This is confirmed by inhibition of the reaction with galvinoxyl and duroquinone, by the initiating effects of azodiisobutyronitrile and benzoyl peroxide, and by the fact that chiral substances are racemised.[26]

$$\left.\begin{array}{l} Q^{\cdot} + Ir(I) \rightarrow Ir(II)-Q \\ Ir(II)-Q + R-X \rightarrow X-Ir(III)-Q + R^{\cdot} \end{array}\right\} \text{initiation}$$

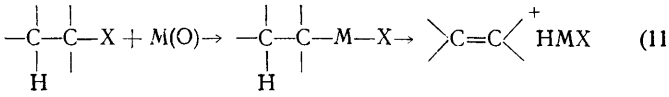
$$\left.\begin{array}{l} R^{\cdot} + Ir(I) \rightarrow R-Ir(II) \\ R-Ir(II) + R-X \rightarrow R-Ir(III)-X + R^{\cdot} \text{ etc.} \end{array}\right\} \text{chain extension} \qquad (9)$$

The stereochemistry of reaction (9) was studied using racemic diastereoisomers and pure enantiomers.[27]



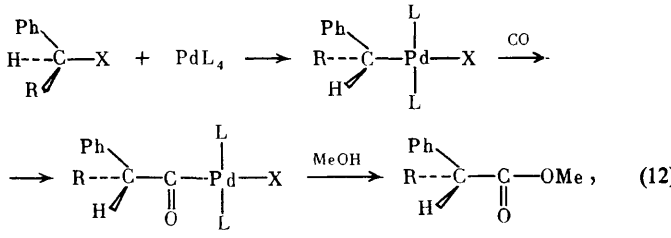
(10)

Oxidative addition involving d^{10} platinum and palladium complexes proceeds by an even more complicated pathway than reaction with Ir(I) complexes.[28] Alkyl halides which do not possess a β-hydrogen atom react with zero-valent palladium complexes to give stable alkylpalladium complexes.[29] However, with halides which do have a β-hydrogen atom, β-elimination of metal hydride takes place and the σ-alkyl complex is not isolated.



(11)

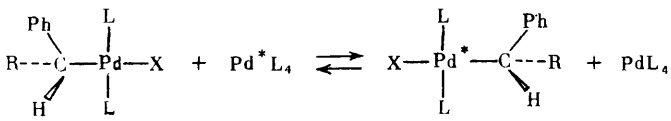
An S_N2-type mechanism prevails for reactions with palladium complexes since chiral benzyl halides react predominantly with inversion of configuration at the benzylic carbon atom.[30] Both primary and secondary benzyl halides react according to this mechanism.



(12)

R = D, CH_3; L = PPh_3.

It has been suggested that the observed partial racemisation is a consequence of a metal–metal exchange involving Pd(0) and Pd(II) complexes, rather than intervention of a radical process.[30]



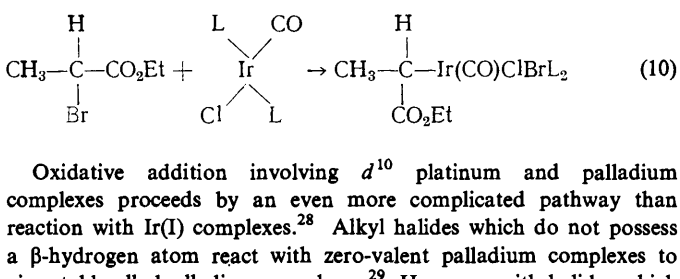
(13)

Alkylation of palladium complexes having the more basic phosphine ligand, L = PEt_3, also proceeds with inversion of configuration, but the optical yield is relatively low.[31]

With such halides as 9-bromofluorene, α-carbethoxybenzyl bromide, and trimethylsilylchloride, the corresponding dimers are obtained, rather than products derived via oxidative addition:[29]

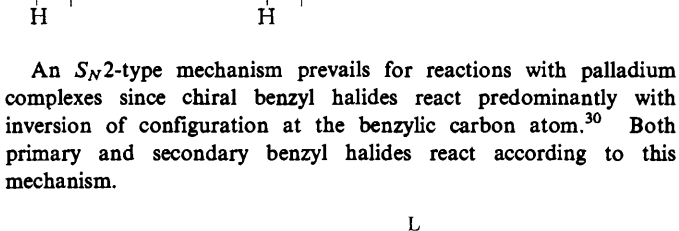
$$2RX + PdL_4 \xrightarrow[-2L]{} R-R + PdX_2L_2. \qquad (14)$$

In contrast to palladium(0) complexes, platinum(0) analogues react with organic halides essentially by a radical mechanism.[28,32,35] Thus, the reaction of n-butyl bromide with $Pt(PEt_3)_3$ is inhibited by galvinoxyl. It has been reported, in fact, that galvinoxyl interacts with a Pt(0) complex.[28] Methyl iodide reacts with $Pt(PEt_3)_3$ via oxidative addition, the process being overall of the second order. The interception of free radicals by radical traps, such as tert-BuNO', is indicative of the participation of radical intermediates.[28] A radical-chain process is proposed for such reactions involving a one-electron transfer step.[28]



$n = 2, 3$: RX = MeI, $MeCH_2I$: L = PPh_3. (15)

A mechanism involving an initial complex formation between halide and complex, $M(0)L_n$, is involved for reactions of unsaturated organic halides.[34]



(16)

Contrasting with nucleophilic aromatic substitution,[35] the reactivity of aryl halides decreases in the following order: I > Br > Cl. Electron-accepting substituents in the aromatic ring facilitate oxidative addition.[36]

Oxidative addition of aryl halides to zero-valent nickel complexes leads to the formation of a paramagnetic Ni(I) complex in addition to a *trans*-arylnickel(II) halide.[37,38] The proportion of each depends on the nature of the halogen in ArX, the type of ring substituent, and the solvent. The reaction is overall of the second order. It is proposed that the rate-determining stage is the one-electron oxidation of the Ni(0) complex with the aryl halide; the radical-ion pair thus formed reacts by two independent pathways affording the product of oxidative addition and an Ni(I) complex. It is possible that the electron transfer step precedes π-complex formation between the reactants.

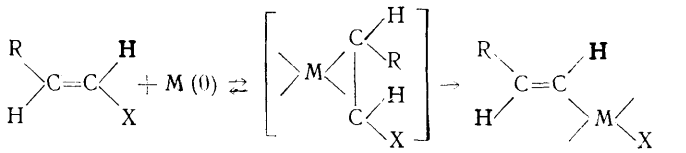


(17)

It should be pointed out that Ni(I) complexes may react with aryl halides with the formation of arylnickel(III) complexes; however, this reaction proceeds far more slowly than the reaction of ArX with an Ni(0) complex. According to one report,[38] oxidative addition to Ni(I) is the key step in the synthesis of biaryls from aryl halides in the presence of nickel complexes and metallic zinc.

$$Ni^{I}X + ArX \rightarrow ArNi^{III}X_2,$$
$$ArNi^{III}X_2 + ArNi^{II}X \rightarrow Ar_2Ni^{III}X + NiX_2,$$
$$Ar_2Ni^{III}X \rightarrow Ar{-}Ar + Ni^{I}X. \quad (18)$$

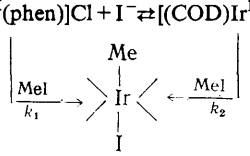
The reaction of vinyl halides with Pt-, Pd-, and Ni-complexes takes place with retention of the (*E*) or (*Z*)-configuration of the unsaturation, leading to the corresponding σ-vinylmetal complex.[39–44] It is proposed[44] that oxidative addition precedes formation of a π-olefin complex. Such a complex has, in fact, been isolated, and characterised, from the reaction of perhalogenoethylenes with Pt(0).[45]


(19)

It is unlikely that oxidative addition of vinyl halides proceeds via formation of free radicals as vinyl radicals readily undergo configurational isomerisation.[46]

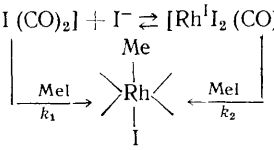
There are several examples of anionic catalysis in oxidative addition.[47–49] The coordination of anions, such as iodide ion, leads to the formation of anionic complexes which display significantly higher activity than the corresponding uncharged complexes in oxidative addition. Of the two examples shown below, the second provides the basis of the industrial synthesis of acetic acid (Monsanto).

$$[(COD)Ir^{I}(phen)]Cl + I^- \rightleftarrows [(COD)Ir^{I}(phen)I]^-$$


(20)

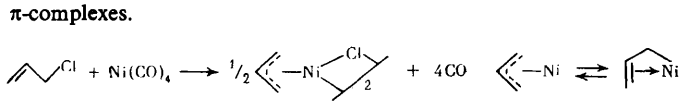
$$k_2 \simeq 7k_1$$

$$[Rh^{I}I(CO)_2] + I^- \rightleftarrows [Rh^{I}I_2(CO)_2]^-$$

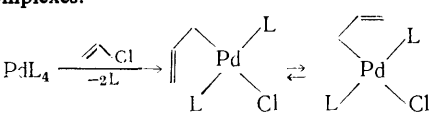

(21)

$$k_2 > k_1$$

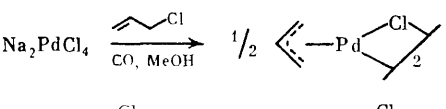
Allyl halides are more active than alkyl, vinyl or aryl halides in oxidative addition. They readily react with nickel, palladium and platinum complexes even in the absence of strong donor ligands. Thus, nickel tetracarbonyl interacts with allyl halides to produce dimeric π-allyl complexes.[50] According to PMR data, a mobile equilibrium is established between the corresponding σ- and π-complexes.

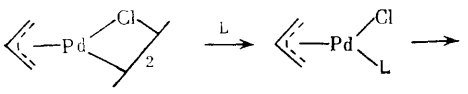

(22)

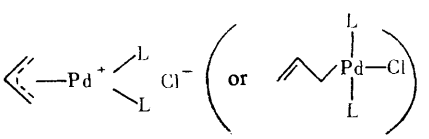
The reaction of allyl chlorides with tetrakis(triphenylphosphine)-palladium(0) leads to the formation of an equilibrium mixture of allyl complexes.[51]


(23)

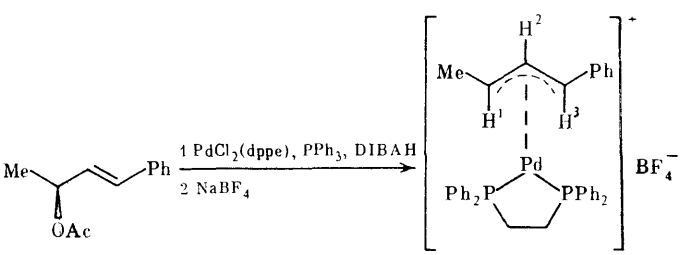
Palladium(0), generated by reduction of Pd(II) salts, interacts with allyl chlorides to give the corresponding bis(π-allylpalladium chlorides).[52] Treatment of the latter with excess of phosphine affords either a cationic π-allyl complex or a σ-complex, depending on the nature of the solvent.[51]


(24)



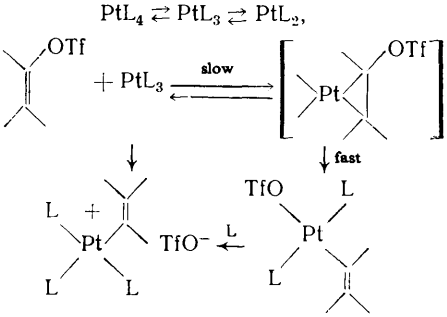

(25)

Oxidative addition of allylic substrates to zero-valent palladium complexes proceeds with inversion of configuration.[53]

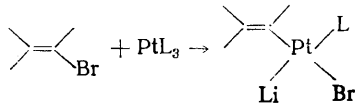

(+)-(1*R*, 2*S*, 3*S*) (26)

Substrates having a leaving group other than halogen may also participate in oxidative addition; however, such reactions have been studied relatively little. There are, however, a large number of catalytic reactions of organometallic compounds with organic triflates,[54] phosphates,[55] with simple and allylic silyl enol ethers,[56,57] and sulphides,[58] tellurides,[59] and with selenides.[60] The mechanism of the reaction of vinyl triflates with zero-valent platinum complexes has been studied.[61] On the basis of a detailed product analysis, a study of the kinetics and stereochemistry of the reaction, a comparison of the reactivity of structurally diverse vinyl triflates, and an NMR study of intermediates, the mechanism of the reaction would appear to involve formation of a vinyl triflate π-complex with Pt(0).

$$PtL_4 \rightleftarrows PtL_3 \rightleftarrows PtL_2,$$

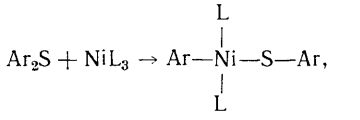

(27)

It should be pointed out that neutral complexes are obtained on reaction of vinyl bromides with PtL_3, rather than cationic complexes as are formed with vinyl triflates.



(28)

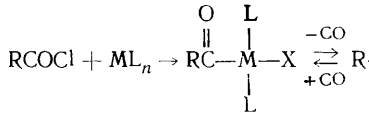
The interaction of diaryl sulphides with tris(tri-n-butylphosphine)-nickel leads to products of oxidative addition across the carbon–sulphur bond, as evident from NMR data and X-ray structural analysis.[62]



(29)

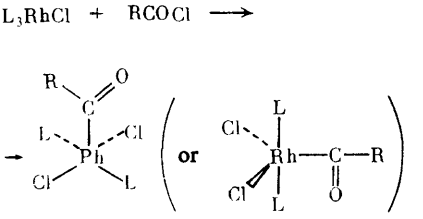
Ar = *p*-$MeOC_6H_4$, C_6F_5; L = n-Bu_3P.

Acyl chlorides also take part in oxidative addition with zero-valent nickel, palladium and platinum complexes.[63,64] Subsequent decarbonylation takes place most easily with nickel complexes.



(30)

Depending on the structure of the acyl group, reaction of acyl chlorides with Rh(I) complexes yields square-pyramidal or trigonal-bipyramidal complexes.



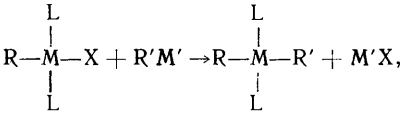
(31)

Rearrangement of acyl to carbonyl complexes proceeds reversibly ($k_1/k_{-1} = 7\times10^{-2}$) where R = $C_6H_5CH_2$, and irreversibly where R = Ar.[65,66]

The d^8 complexes of the nickel triad formed by oxidative addition may react further with organic halides to produce the corresponding d^6 complexes. There are many examples where such complexes are formed with Pr(II),[67] and complexes of the type *fac*-L_2PtIMe_3 have been isolated and characterised. A Pd(IV) complex with three σ-bonded methyl groups, *fac*-[$PdMe_3$(2,2′-bipyridyl)I], has also been prepared for the first time and characterised structurally.[68]

III. Transmetallation

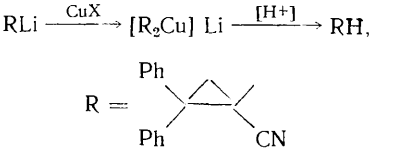
Transmetallation is the next step of the catalytic cycle in the cross-coupling of organometallic compounds with organic halides. In the process the halogen atom in the complex $RMXL_2$ is replaced by the organic residue, R′, of the organometallic compound



(32)

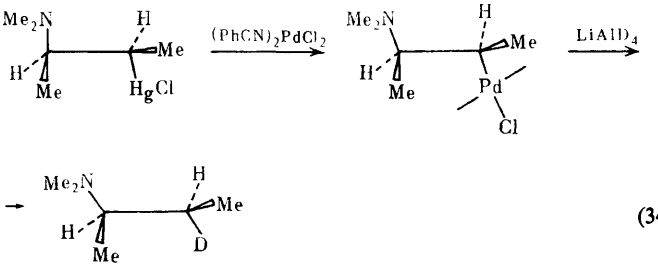
M = Ni, Pd; M′ = Li, Mg, Zn etc.

Transition metal complexes with σ-bonded organic residues may be generally prepared via transmetallation. It involves the interaction of a transition metal halide with an organometallic compound of a non-transition element to produce a transition metal compound with one or more σ-bonded organic groups.[21] The detailed mechanism by which the organic residue of the organometallic compound is transferred to the transition metal has not, as yet, been established; however, in a number of cases, it has been shown that this process takes place stereospecifically. Thus, the cyclopropyl group of lithiated cyclopropanes is transferred to copper with retention of configuration.[69]



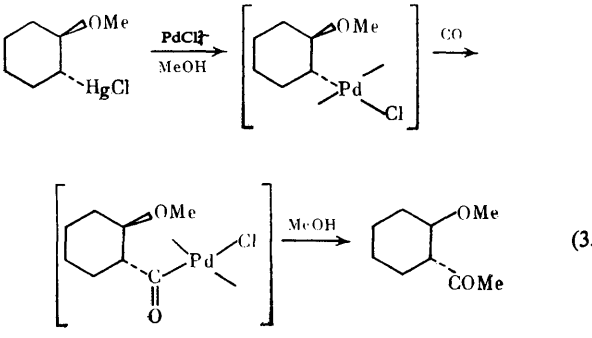
(33)

Organomercury compounds are widely used for the preparation of transition metal complexes.[70] Mechanistically, the reaction involves electrophilic cleavage of the mercury–carbon bond with the transition metal halide. The alkyl group of the organomercury compound transfers to Pd(II) with retention of configuration, as shown in the reactions of the *erytho*- and *threo*-isomers of β-amino-ethylmercury chlorides with bis(acetonitrile)dichloropalladium(II).[71]



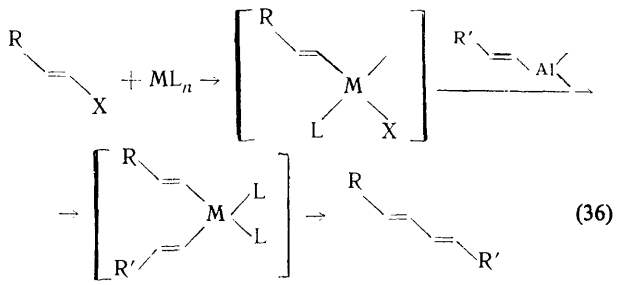
(34)

Retention of configuration on transmetallation is also observed with cyclohexylmercury compounds.[72]



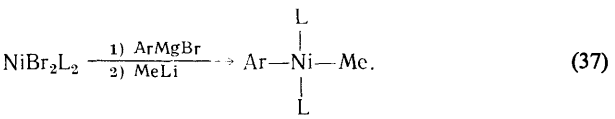
(35)

The configuration at the sp^2 carbon atom is retained at all stages of the catalytic cycle, as illustrated in the reactions of vinylalanes with vinyl halides catalysed by nickel and palladium complexes.[73]



(36)

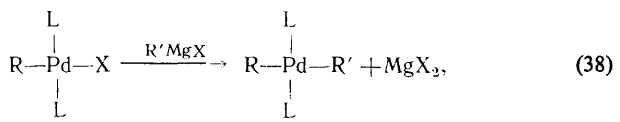
Nickel(II) complexes with two σ-bonded organic groups have also been obtained by transmetallation.[74]



(37)

L = PEt_3

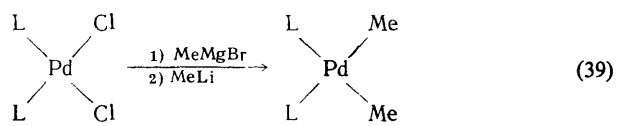
The *trans*-configuration of the nickel complexes has been confirmed by a ^{31}P NMR study.[74] Complexes of the type, *trans*-$RPdR'L_2$, have been isolated by reaction of Grignard compounds with $RPdXL_2$ complexes obtained by oxidative addition of RX to Pd(0).[19,75]



(38)

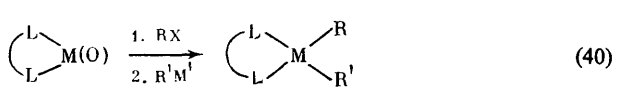
L = PEt_2Ph, PEt_3.

The corresponding *cis*-palladium complexes have been prepared from *cis*-$PdCl_2L_2$ by sequential transmetallation with organomagnesium and -lithium compounds.[76]



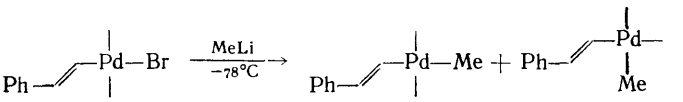
(39)

Nickel and palladium complexes with bidentate, configurationally locked, ligands may react sequentially with organic halides and organometallic compounds with the formation of the corresponding *cis*-diorgano-complexes.



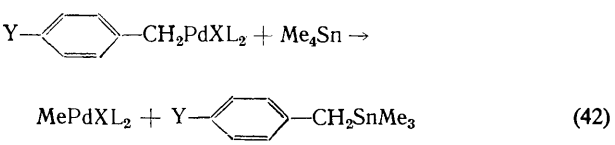
(40)

By a ^{31}P NMR study,[77] it has been shown that transmetallation of palladium *trans*-(*E* or *Z*)-styryl complexes with methyllithium leads to a mixture of *trans*- and *cis*-methyl(styryl)palladium complexes.



(41)

The interaction of benzylpalladium(II) complexes with tetramethyltin in HMPA at 25 °C results in exchange of the benzyl group by methyl, rather than exchange of a halogen atom on the metal.[78]



(42)

The interaction of organolithium compounds with L_2PdCl_2 complexes leads to tri- and tetra-organopalladates.[79] The resistance of the latter to reductive elimination (see below) is evidently the reason why lithium acetylides are inert towards cross-coupling.[15]

IV. Reductive elimination

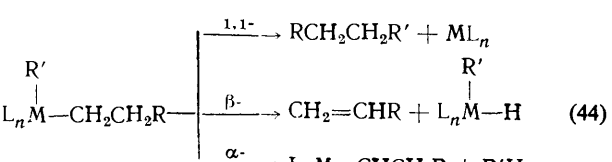
Reductive elimination, the reverse of oxidative addition, proceeds with formation of a bond between ligands X and Y and reduction of the coordinated metal. This type of conversion is particularly important because it results in the liberation of the desired organic product in the final step of the catalytic cycle of the cross-coupling. The same process is involved in the majority of other homogeneous catalytic reactions.



(43)

In an earlier review,[80] the basic features of reductive elimination, namely the associated formation of carbon–carbon, carbon–hydrogen and carbon–heteroatom bonds, have been outlined. Here we shall focus primarily on that process by which the carbon–carbon bond is formed.

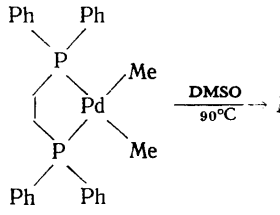
β-Elimination is notably prevalent with transition metal alkyl complexes. If this elimination is not possible (where, for example, there is no β-hydrogen atom, or where a free coordination site on the metal complex is not available, etc.), the complex undergoes α-elimination or 1,1-reductive elimination.



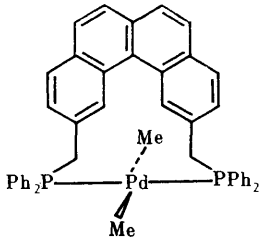
(44)

1,1-Reductive elimination of two organic residues with subsequent formation of a new carbon–carbon bond is the key step in catalytic cross-coupling. Before reductive elimination takes place, the ligands must be *cis*-oriented. As seen in the examples below, ethane is

readily eliminated from two *cis*-oriented methyl ligands, while *trans*-oriented groups fail to react.[76]



$$\xrightarrow[90^\circ C]{DMSO} Me{-}Me \qquad (45)$$



$$\xrightarrow[100^\circ C]{DMSO} \text{no reaction} \qquad (46)$$

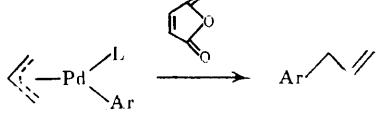
The rate of reductive elimination is increased if there is a positive charge on the complex. Thus, the Pt(IV) complex, $PtL_2Ph_2I_2$, is stable in benzene but readily eliminates iodobenzene in methanol. Evidently, the cationic complex formed by dissociation of iodide ion eliminates iodobenzene far more readily than the corresponding neutral complex.[81]

$$\begin{array}{ccc} PtL_2Ph_2I_2 & \overset{MeOH}{\rightleftharpoons} & [PtL_2Ph_2I\,(MeOH)]^+I^- \\ \downarrow PhH & & \downarrow -PhI \\ \text{no reaction} & & [PtL_2Ph\,(MeOH)]^+I^- \\ & & \downarrow \\ L = PEt_3 & & PtL_2PhI \end{array} \qquad (47)$$

An oxidant may be employed to initiate reductive elimination. It has been shown, for example, that ethylene and ethane are isolated as the initial elimination product by thermolysis of the neutral complex, $Et_2Fe(bipy)_2$;[82] however, rapid and selective formation of butane can be achieved by 2-electron oxidation of the complex by electrochemical means or on treatment with $[IrCl_6]^{2-}$.

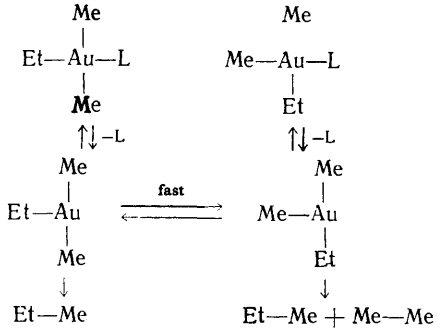
$$Et_2Fe\,(bipy)_2 \xrightarrow{-2e^-} n\text{-}C_4H_{10}. \qquad (48)$$

Even the formation of charge-transfer complexes with electron-deficient olefins may initiate elimination of alkane from dialkyl complexes of the type $Et_2Ni(bipy)$.[83] Thus, olefins such as maleic anhydride and tetracyanoethylene induce reductive elimination from palladium π-allyl complexes with formation of coupling products of the type allyl–allyl and allyl–aryl.[84,85]



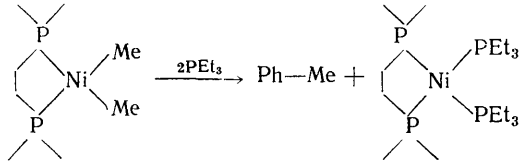
(49)

The accelerating effect of the positive charge does not require any further explanation since reductive elimination is, in itself, a process involving oxidation by the metal atom—in this case oxidation of two organic ligands. In the process by which the ligands (even the neutral ones) are dissociated, there is an increase in the actual positive charge on the metallic centre, and the rate of reductive elimination increases. Planar gold complexes of the type R_3AuL undergo reductive elimination through formation of tri-coordinate *T*-shaped intermediates. Because *cis*- and *trans*-$EtMe_2AuL$ afford a mixture of ethane and propane in equal amount, it follows that *T*-shaped complexes isomerise more readily than undergo elimination of R–R.[86]

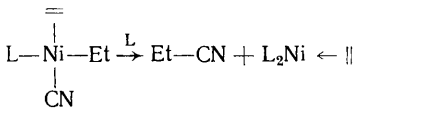


(50)

However, some reductive eliminations do not require preliminary dissociation of the ligand. Examples are known wherein elimination is enhanced if coordination of another ligand takes place.[87,88]



(51)



(52)

According to one report,[74] two concurrent processes are involved in the reductive elimination of planar nickel complexes of the type $ArNiMe(PEt_3)_2$. A dissociative mechanism is at play during thermolysis of the complex, by which a preliminary cleavage of the ligand takes place.

$$ArNiMeL_2 \rightleftarrows ArNiMeL + L,$$

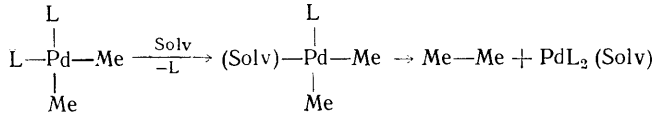
$$ArNiMeL \rightarrow Ar{-}Me + NiL. \qquad (53)$$

Aryl halides induce the second step which involves a radical-chain process with the participation of paramagnetic Ni(I) and Ni(III) species. The radical character of this step is indicated by the formation of radical products, by an induction period, and by the strong influence of promoters and inhibitors on the reaction rate.

$$\left.\begin{array}{l} ArNiMe \xrightarrow{\Delta} ArMe + Ni^0, \\ ArX + Ni^0 \rightarrow Ar^{\cdot} + Ni^{I}X, \\ Ar^{\cdot} + Ni^0 \rightarrow ArNi^{I}, \end{array}\right\} \text{initiation}$$

$$\left.\begin{array}{l} ArNi^{I} + ArX \rightarrow Ar_2Ni^{III}X, \\ Ar_2Ni^{III}X + ArNi^{II}Me \rightarrow ArNi^{II}X + Ar_2Ni^{III}Me, \\ Ar_2Ni^{III}Me \rightarrow ArMe + ArNi^{I} \text{ etc.} \end{array}\right\} \text{chain extension} \qquad (54)$$

The key characteristics of reductive elimination have been studied in detail with palladium complexes, R_2PdL_2. Thus, it has been established that elimination of ethane from *cis*-Me_2PdL_2 is a first-order reaction involving a dissociative mechanism.[89]

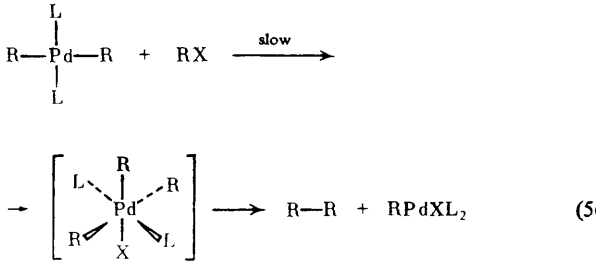


Solv – solvent

(55)

This mechanism is in accord with theoretical calculations for the reductive elimination of ethane from bis(phosphine)dimethylpalladium complexes.[90] The main conclusions drawn from these calculations are the following. Strong donor ligands *trans* to a methyl group hinder elimination. Reductive elimination of ethane from 4-coordinate complexes, *cis*-Me_2PdL_2, is allowed by symmetry, and determined by the energy of the antisymmetrical b_2 orbital of the palladium complex. The value of the energy barrier for elimination from palladium complexes is far higher than the corresponding value for nickel complexes in which the energy of the b_2-orbital is lower. The activation energy for elimination of ethane from 3-coordinate *T*- and *Y*-shaped intermediates is less than that for complexes Me_2PdL_2. The energy barrier for isomerisation from one *T*-structure to another is significantly greater than the barrier for elimination from *T*- and *Y*-shaped complexes (compare reductive elimination of R–R from R_3AuL [50]).

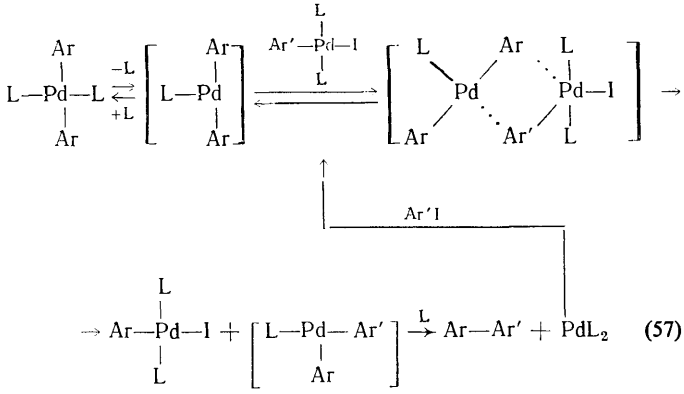
The foregoing explains why *trans*-R_2PdL_2 complexes, which routinely participate in catalytic cross-coupling, must initially isomerise into *cis*-R_2PdL_2. A coordinating solvent (THF, DMSO, DMF) of an additional phosphine ligand is required for isomerisation, i.e. *trans-cis* isomerisation takes place by an associative mechanism.[76] If *trans-cis* isomerisation is not possible for steric reasons, then the complexes resist reductive elimination.[46] Yet *trans*-Me_2PdL_2 complexes do react with CD_3I, even at 20 °C, to give 1,1,1-trideuterioethane exclusively.[76] Added CH_3I also increases the rate of formation of ethane from *cis*-dimethylpalladium complexes.[89] According to certain authors,[89] these data confirm that reductive elimination from R_2PdL_2 in the presence of organic halide proceeds through intermediate formation of palladium(IV) intermediates.



(56)

There is, in fact, one report on the isolation and full characterisation of a Pd(IV) complex, *fac*-$Me_3PdI(bipy)$.[68] The possible participation of Pd(IV) intermediates has been critically evaluated.[91]

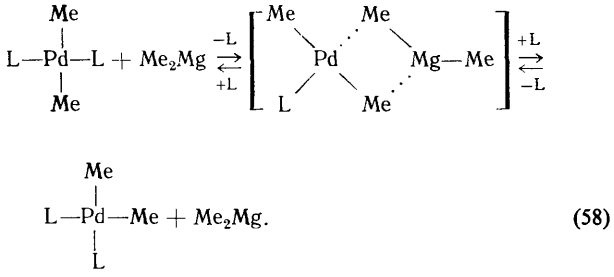
According to another report,[92] the rate of reductive elimination of biaryls from *trans*-Ar_2PdL_2 in the presence of aryl iodide is not dependent on the intermediate formation of a Pd(IV) complex, but rather on the facile isomerisation of *trans*-Ar_2PdL_2 into the *cis*-complex under the influence of *trans*-$Ar'PdIL_2$, obtained by oxidative addition of Ar'I to the Pd(0) complex.



(57)

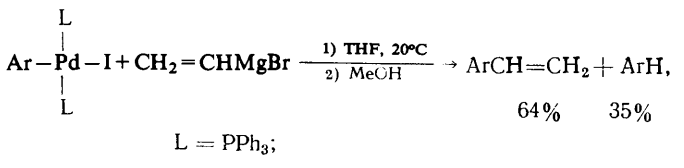
The catalysed isomerisation of Ar_2PdL_2 by $Ar'PdIL_2$ is accompanied by a profound reorganisation of organic residues, leading to the formation of three types of biaryl: ArAr', Ar_2 and Ar'_2.[92]

However, under the conditions for catalytic cross-coupling with organomagnesium compounds ($RX:R'MgX:PdL_n$ = 1:1.5:0.01), the process shown in Eqn. (57) is unlikely because $RPdXL_2$ complexes readily react with R'MgX to give $RPdR'L_2$. At the same time, it has been shown that *trans-cis* isomerisation proceeds readily on treatment with organomagnesium compounds.[79]



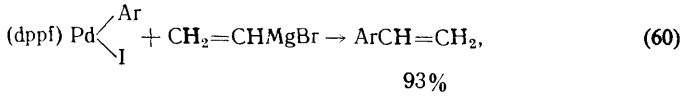
(58)

In this context, it is unlikely that *cis-trans* isomerisation would take place in the presence of organomagnesium compounds under the conditions of the actual catalytic cycle of the cross-coupling between RX and R'MgX. The following data (schemes 59 and 60), taken from a product analysis[93] of the reaction of *trans*-$ArPdIL_2$ and *cis*-ArPdI(dppf) [where dppf is 1,1'-bis(diphenylphosphino)-ferrocene] with vinylmagnesium bromide ($ArPdIL_2:CH_2=CHMgBr$ = 1:100), support this contention.



L = PPh_3;

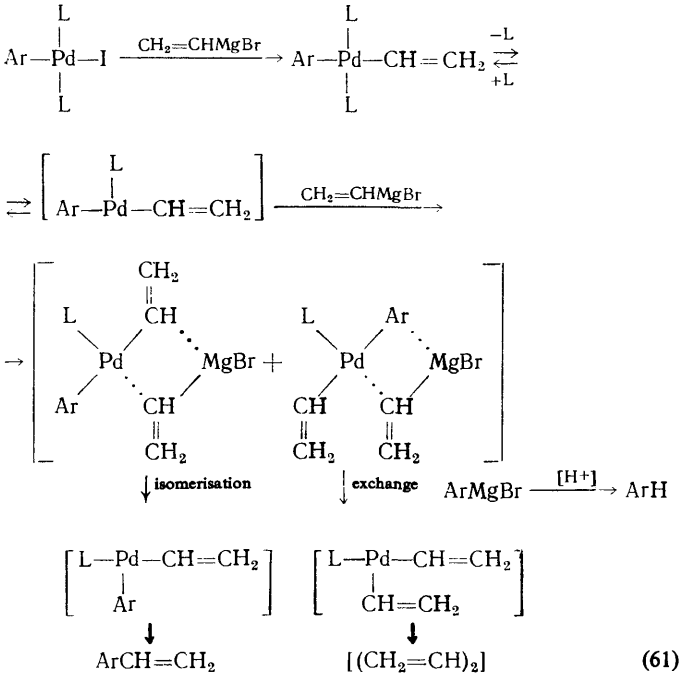
(59)



Ar = *p*-PhC_6H_4.

(60)

It should be pointed out that the corresponding catalysed reaction of *p*-iodobiphenyl with $CH_2=CHMgBr$ leads to the same type of products. The results are summarised in scheme (61). Here, the interaction of a *trans-T*-type intermediate, $ArPd(CH=CH_2)L$, with vinylmagnesium bromide is critical. This takes place by two independent routes: via *trans-cis* isomerisation and via exchange of organic residues beteween the organopalladium and organomagnesium compounds.



(61)

If the *trans-cis* isomerisation had taken place with the participation of the complex $ArPdIL_2$, then the tetraphenyl *p*-quaterphenyl would have been present in the reaction product.[59]

The absence of side-products from reactions involving palladium complexes with bidentate ligands, by which mono- and diorganocomplexes are formed with the *cis*-configuration, would suggest that transmetallation and subsequent reductive elimination take place in such cases far more readily than the exchange process.

V. The influence of the ligand environment in the transition metal complex on the efficiency of cross-coupling

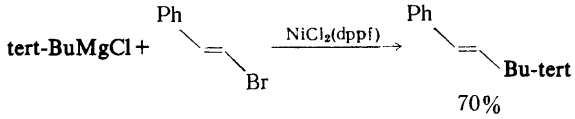
The correct choice of ligand for the nickel of palladium complexes is critical for the cross-coupling to succeed. A comparison has been made of various nickel complexes as catalysts for the reaction of chlorobenzene with n-butylmagnesium bromide.[94]

$$PhCl + n\text{-}BuMgBr \xrightarrow{NiCl_2L_2} n\text{-}Bu-Ph \quad 81—100\% \qquad (62)$$

L_2 = dppp[1,3-bis(diphenylphosphino)propane], dmpf[1,1′-bis(dimethylphosphino)ferrocene].

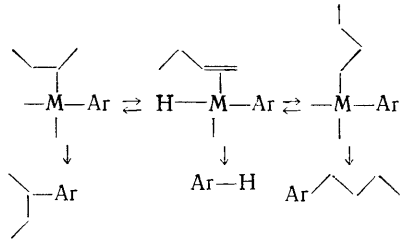
Nickel complexes with other phosphine ligands have little catalytic activity.[62] Generally speaking the choice of ligand is governed by the structure of the organic residue in RX and R′MgX.[94]

For cross-coupling of n-, *sec*- and tert-alkylmagnesium halides with aryl and vinyl halides, it has been shown that nickel and palladium catalysts with the bidentate ligand, 1,1′-bis(diphenylphosphino)ferrocene (dppf), are selective and afford the desired products in high yield.[95,96]



(63)

The correct choice of ligand is especially important in the alkylation of aryl halides where isomerisation of *sec*-alkyl groups and reduction of ArX to ArH could complicate the desired cross-coupling. The mechanism of these side reactions, i.e. isomerisation and reduction, has been examined [97] (see scheme 64).



(64)

The absence of side-products when dppf is used as ligand confirms that, in this case, reductive elimination with the formation of *sec*-BuAr proceeds significantly more rapidly than β-elimination.

Thus selectivity and catalytic activity of palladium complexes with bidentate bis(diphenylphosphino) ligands depends on the distance between the two diphenylphosphino groups.[98] For alkylation in the presence of bis(diphenylphosphino)palladium complexes, selectivity increases as the P—Pd—P bond angle increases in the sequence dppe < dppp < dppf, and as the Cl—Pd—Cl bond angle decreases in the sequence dppe > dppp > dppf. As is the case with *cis*-(*sec*-Bu)$PdArL_2$ complexes, the increase in selectivity (in the order dppe < dppp < dppf) is, in all likelihood, associated with the increased rate of reductive elimination, determined by the more facile approach of the organic residues.

It has been shown that nickel complexes with bi- and tetra-dentate ligands (β-diketones, β-ketothiones, β-ketoimines, amino-acids, diamines, etc.) exert a high catalytic activity in the reactions of aryl-Grignard compounds with aryl halides.[99]

$$PhMgBr + o\text{-}PhC_6H_4I \xrightarrow{«Ni»} o\text{-}PhC_6H_4Ph \quad \text{up to } 90\% \qquad (65)$$

Recently, $PdCl_2$(dppf) was shown to have high catalytic activity in the reactions of alkylboron compounds with aryl and alkenyl halides.[100]

In conclusion, it should be pointed out that, of all the catalysts used at the present time in cross-coupling, $PdCl_2$(dppf) is the most versatile by virtue of its high activity and selectivity.

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Metal complex catalysis in the chemistry of solid organic raw material

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ABSTRACT. The applications of metal complexes in processes involving the conversion of solid organic raw material is examined. Data are presented on the use of metal complex catalysts for the preparation of organic compounds, synthetic fuels, and cellulose and its derivatives from coal and plant biomass.

The bibliography includes 81 references.

Contents

I. Introduction 1185
II. Characteristics of the catalytic reactions of solid organic raw material 1185
III. Synthesis of organic compounds from coal and biomass 1186
IV. Preparation of cellulose from wood 1187
V. Preparation of synthetic fuels 1189

I. Introduction

The principal sources of natural raw materials are petroleum, natural gas, coal, oil shale, and plant biomass. At the present time the world production of petroleum and natural gas approaches the maximum possible amount and in the near future will begin to fall. In order to overcome the deficiency of petroleum raw material, it is planned in the industrially developed countries to manufacture synthetic hydrocarbon fuels from coal, the available amount of which greatly exceeds that of petroleum and gas. Almost all the most important petrochemical products can be obtained by the chemical processing of coal. Two aspects of the preparation of synthetic fuels and chemical products from coal are most promising: liquefaction and gasification. The liquid and gaseous products formed thereby are subjected to further conversion into motor fuels and valuable organic substances.

Plant biomass is a continuously renewed source of organic raw material. Photosynthesis generates annually about 200 billion tons of biomass on our planet, which greatly exceeds the world production of mineral organic fuels. Chemical wood conversion processes have as a rule two principal aims: the isolation of individual components of wood (for example, cellulose) or the depolymerisation of wood with formation of lower-molecular weight products (for example, sugars and furfural). Not only the entire set of compounds which are nowadays synthesised from petroleum but also a whole series of unique products, for example biologically active substances, can be obtained from primary products of plant origin. The preparation of synthetic liquid and gaseous fuels from the plant biomass is promising.

The majority of the methods for the chemical conversion of coal and biomass used at present are less efficient than petrochemical processes. The solid organic raw material is less susceptible to conversion into low-molecular-weight products than petroleum and requires more severe reaction conditions. In order to intensify the coal and biomass conversion processes, catalysts developed initially for the conversion of liquid and gaseous organic raw material are being used on an increasing scale.[1,2] However, the possibilities of traditional catalysis in this field are limited by the difficulty of ensuring a sufficiently close contact between the solid raw material and the catalysts. It is therefore useful to use liquid catalytic systems capable of penetrating into the pores of the solid organic reactant. Many reactions occurring in the chemical conversion of coal and plant biomass include, together with heterolytic stages, also homolytic stages. In order to accelerate the latter, one can use a wide range of metal complex catalysts or bifunctional catalytic systems in solution. There exist fairly numerous examples of the effective employment of metal complex catalysts for the acceleration and increase in the selectivity of the synthesis of organic compounds from coal and wood and also for the improvement of processes leading to the formation of synthetic fuels. The introduction of metal complexes into the pores of the organic raw material or their fixation on the surface is also used on an increasingly wide scale to effect energochemical solid fuel conversion processes (gasification, pyrolysis, liquefaction). Metal complexes are frequently used in this connection as precursors of highly dispersed particles formed at elevated temperatures.

This review deals with certain aspects of the application of metal complex catalysts in the chemistry of solid organic raw material and an attempt is made to give a systematic account of the experimental data obtained during the last 5–8 years in this non-traditional field of catalysis.

II. Characteristics of the catalytic reactions of solid organic raw material

The use of catalysts to convert solid organic raw material has a number of features distinguishing it from the traditional conversion reactions of liquid and gaseous products.[3] In the technological application of catalytic solid fuel conversion processes, it is essential to take into account the characteristic features of the composition and structure of the fuel.

1. Composition and reactivity of different types of coal and wood

According to generally accepted ideas, the organic mass of coal consists of condensed aromatic nuclei linked via aliphatic side groups, which include carbon, hydrogen, oxygen, sulphur, and nitrogen atoms.[4,5] Oxygen-containing groups promote the formation

of bonds between organic and inorganic components of coal. Such groups are present in phenols, alcohols, ethers, carboxylic acids, and carbonyl compounds. The structure of the vitrinite component of coal, whose amorphous macromolecular lattice consists of a series of stable cluster units or aggregates linked by relatively weak bridges made up of aliphatic carbon atoms or by ether bridges as well as weak hydrogen or donor–acceptor bonds, has been studied in greatest detail.

Overall, natural types of coal have a much more complex chemical composition than petroleums. The molecular groups forming part of coal are to a large extent linked to one another by chemical bonds. The aim of the chemical processing of coals is their depolymerisation with formation of low-molecular-weight products which would have a homogeneous composition. The conversion of coal into individual organic compounds to which the chemist is more accustomed is achieved by heat treatment and treatment with various reagents. This entails in the first place the rupture of weakest aliphatic chains linking the condensed aromatic structures and donor–acceptor bonds.

Wood biomass consists mainly of cellulose (40–50%), lignin (16–33%), and hemicelluloses (15–30%). The remaining small fraction consists of extractable substances and inorganic components.[6] The most valuable substance in wood, namely cellulose, is a linear polysaccharide made up of $C_6H_{10}O_5$ units linked by 1–4 glycosidic bridges. Hemicelluloses are polysaccharides with shorter chains made up of $C_5H_8O_4$ units. Lignin is less reactive than cellulose and hemicelluloses. Among all the components of wood, it is closest in its composition and properties to brown coal. The aromatic structures of lignin are believed to include combination of phenylpropane structural units linked by ether or carbon–carbon bonds.

The characteristics of the structure and reactivity of the components of coal and biomass must be taken into account in selecting the optimum procedures for the introduction of catalysts into the solid organic raw material.

2. Applications of metal complex catalysis

It is useful to distinguish the following aspects of the use of metal complexes to effect the catalytic conversions of solid organic raw material: catalysis by soluble metal complexes introduced into the pores of the organic substance; catalysis by metal complexes fixed on the surface of the solid reactant; catalysis by highly dispersed particles or clusters formed on decomposition of the metal complexes introduced into the raw material or fixed on its surface.

The possible applications of metal complexes in solution are limited by the threshold of their thermal stability (in most cases 150–200 °C). The mechanism of the catalytic conversion can include a stage in which the metal complex is adsorbed on the reactive sections of the surface of a solid organic raw material. Catalytic reactions can also take place in solutions where metal complexes accelerate the reactions of the products of the thermal fragmentation of coal or of the components of the biomass.

If the catalyst accelerates the conversion of liquid or gaseous substituents of the reaction mixture without interacting at the same time with the solid raw material, an atypical pathway can be achieved in the catalytic process. Catalytic reactions of this type are an example of mediated catalysis, which is being used on an increasingly wide scale in the conversion reactions of coal and plant raw material.

The closest contact between the raw material and the catalyst can be achieved by binding catalytically active metal complexes to the surface reactive groups of coal and wood such as phenolic, acid, aldehyde, and lactone groups. They all enter into the composition of cellulose, lignin, and other components of wood, which leads to extensive possibilities for a uniform distribution of catalytically active compounds in the solid raw material.

The methods for the chemical fixation of metal complexes on the surfaces of oxide and polymeric carriers have been thoroughly developed.[7–9] There are also data concerning the fixation of various transition metal compounds on cellulose materials. Thus cations can be arranged in the following sequence in terms of their ability to be sorbed by cellulose: $Cd^{2+} > Zn^{2+} > Cu^{2+}$.[10] The maximum sorption capacity of the Cd^{2+} cations is due to their high polarisability. In an acid medium, the exchange adsorption of cations increases as a consequence of their being bound to the COOH and SO_3H groups. A reactive oxygen-containing group (e.g. an acid or phenolic group) can be obtained at high concentrations also on the surfaces of different types of coal as a result of special activating treatment.

The metal complexes introduced into the raw material are not only themselves catalysts of the various reactions of coal and the biomass but can also be converted into other catalytically active compounds as a result of thermal and chemical influences. Thus thermally unstable compounds can afford oxide or metallic particles on heating in air or in an inert atmosphere. Hydroxide or oxide compounds can be obtained by treatment with alkali. As an example of the formation of metallic clusters in the cellulose structure, one may refer to a study[11] in which zerovalent metal atoms were introduced into cellulose by dissolving the latter in a copper-ammonia solution which was then extracted by an aqueous solution of alkali. Next, the cellulose, containing up to 16% of Cu^{2+} atoms, was reduced with sodium dithionate or hydrazine; this resulted in the formation of zerovalent copper atoms linked to the cellulose matrix by coordinate bonds. The subsequent treatment of the copper-containing cellulose with solutions containing metal cations with lower electrochemical potentials ($PtCl_2$, $PdCl_2$, H_2PtCl_6) makes it possible to achieve a partial replacement of copper by the atoms of another metal.

III. Synthesis of organic compounds from coal and biomass

The total number of wood conversion products known at the present time exceeds 2500. These are sugars, ethyl alcohol, furfural, laevoglucosan, xylitol, polyhydric alcohols, phenolic derivatives, organic acids, paraffinic hydrocarbons, biologically active compounds, and other products. Many of them are formed in processes involving the hydrolysis, oxidation, and pyrolysis of the solid organic raw material.

The chemicals obtained from coal and plant biomass may in time replace many of the products of petrochemical synthesis.

1. Hydrolysis of cellulose-containing products

The hydrolysis of cellulose-containing products, used to obtain sugars and furfural, includes a multiplicity of a wide variety of reactions, most of which have a heterolytic mechanism. The traditional catalysts of hydrolytic reactions are acids and bases. In order to obtain furfural, it is essential to ensure that pentosans are hydrolysed and the resulting pentoses are dehydrated.

Transition metal compounds can be used as catalysts of the dehydration of pentoses to furfural.[12] Some of them, for example, chromium salts, are 10–15 times more active than sulphuric acid. The combined use of inorganic acids together with metal compounds in many cases both accelerates the formation of furfural and increases its yield.

The catalytic activity of metal complex catalysts can be explained by the formation of metal–sugar complexes, which weakens the intermolecular bonds in pentosans as a consequence of the polarising action of the cation.[12] The catalytic activity of metal complexes increases with increase in the charge on the metal cation, i.e. with increase in its polarising activity. The nature of the ligands is also quite important because metal complexes can undergo partial hydrolysis under the reaction conditions. Anions can then give rise to the corresponding acids, which are capable in turn of influencing the rate of cleavage of polysaccharides and of the dehydration of monosaccharides.

By means of catalysis, it is possible to direct the conversion of the plant raw material via new pathways. Thus in the treatment of aspen wood in a stream of steam at 200–400 °C in the presence of certain transition metal compounds (for example, iron compounds), it has been possible to obtain laevoglucosenone in up to 5 wt.% yield relative to the initial raw material.[13] This compound is promising for the synthesis of valuable substances used in perfumery, medicine, and the food industry.

2. Oxidation and pyrolysis of solid organic raw material

When metal complexes are introduced into a solid organic raw material, the metal cations are frequently bound to the functional groups forming part of the composition of the solid fuel. The same metal ion forming part of the composition of humates can increase the resistance of the substrate to degradation, while in combination with phenoxide ions it can promote the decomposition processes. This leads to the appearance of the possibility of regulating thermochemical conversion reactions of coal and biomass by the selective introduction of metal-catalyst cations into the functional groups of the solid raw material.

There exist examples of the effect of transition metal compounds introduced into coal on the catalytic conversion of the latter into aliphatic polycarboxylic acids.[14] The introduction of iron, manganese, and copper ions as well as metal tungstates and molybdates accelerates the oxidation of wood lignin by hydrogen peroxide which proceeds in an acid medium with decomposition of aromatic rings and the formation of oxalic, malonic, acetic, and formic acids.[15] The oxidation of lignin is accelerated by the potassium hexacyanoferrate(III)/hexacyanoferrate(II) catalytic system; the catalytic effect depends on the potential of the oxidation-reduction system.[17,18]

The catalytic effect of copper chloride was manifested by an increase in the rate of the oxidative ammonolysis of lignin in an aqueous medium or methanol at 127 °C.[16]

Certain metal complex catalysts make it possible to increase the yield of the volatile organic compounds formed in the pyrolysis of wood. Thus the introduction of manganese chloride into wood from deciduous trees increases the yield of laevoglucosan in steam pyrolysis to 10–13.4 wt.% relative to the weight of the absolutely dry wood.[19]

3. Reactions of compounds originating from coal and wood

Organic substances of plant and coal origin have found extensive applications in the national economy. Catalytic processes have been used recently on an increasing scale for their conversion. Some of the most important monosaccharide conversion products are furfural and its derivatives.

Zirconium complexes fixed on a polymeric carrier are effective catalysts of the preparation of furfural by the dehydration of a 2–5% solution of pentoses.[20] The use of the vanadyl-porphyrin complex as the catalyst makes it possible to raise the yield of 5-hydroxymethylfurfural in the conversion of an aqueous solution of sucrose at 90–100 °C.[21] The zirconyl chloride catalyst has also been used to obtain hydroxymethylfurfural from sugars and glucose.[21] In the presence of the titanium sulphate catalyst on a polymeric carrier, the degree of conversion of xylose into furfural reaches 87%.[22] There are data concerning the use of titanium-porphyrin complexes immobilised in a polymer gel in the dehydration of xylose.[23]

It has been suggested that metal chlorides be used as catalysts in the processing of cellulose-containing waste.[24] This makes it possible to hydrolyse part of the cellulose to glucose under mild conditions and the remainder can be converted into wood charcoal.

The reactions of reactive compounds obtained from plant raw material, such as xylitol (a pentahydric alcohol), laevoglucosan (containing a strained anhydride ring and three reactive OH groups), and dioxanorbornene (containing an anhydride ring and a carbon–carbon multiple bond) are also catalysed by dissolved and heterogenised metal complexes.

Valuable products of small-scale chemistry are also obtained in the catalytic processing of extractable substances. The use of catalysts leads to new possibilities for the synthesis of pyrethroids, pheromones, fungicides, and other biologically active substances from the volatile monoterpenoids present in turpentine and also in the essential oils obtained from the bark and green matter of conifers.

An important aspect of the synthesis of organic products from solid organic raw material is the catalytic processing of the mixture of carbon monoxide and hydrogen formed on gasification of coal or biomass. In the presence of heterogeneous Fischer–Tropsch catalysts, mainly complex hydrocarbon mixtures are formed.[25]

The use of metal complex catalysts makes it possible to carry out many reactions leading to the synthesis of individual organic compounds, based on the reaction of CO with molecular hydrogen and other substrates—methanol, formaldehyde, alkenes, dienes, acetylenes, and allyl and chloro-substituted compounds.

The problems of metal complex catalysis in the processing of synthesis gas have been examined in detail in a monograph.[26] Catalysts of a new type used in this field, namely transition metal carbonyl clusters deposited on oxide supports, ensure the formation of individual hydrocarbons (in particular C_2–C_4 alkenes) with a high selectivity at moderate temperatures. When iron and iron-cobalt clusters deposited on silica gel are used, the selectivity in the formation of ethylene or propene reaches 90%.[27]

IV. Preparation of cellulose from wood

1. Delignification of wood in order to obtain cellulose

The delignification of wood is a process involving the removal of lignin from the lignocellulose material by treatment with chemical reagents.[28] The delignification of wood is used to obtain celluloses, which are widely used in industry, especially in the manufacture of paper and chemical fibres.

The results obtained indicate the occurrence of heterolytic and radical reactions in the delignification process. This made it possible to achieve a more specific approach to the selection of catalysts from this process. Catalysts of the oxidation-reduction type based on anthraquinone and its derivatives have been investigated in greatest detail in this process.[29]

There has been a growth of interest recently in the application of metal complex catalysts for the intensification of the preparation of cellulose. Cobalt, manganese, copper, iron, and chromium complexes with organic ligands are used as catalysts in order to replace scarce anthraquinone.[30] The study of the reactions of compounds modelling lignin showed that cobalt and iron complexes with *meso*-tetra-*p*-sulphophenylporphyrin groups promote to a greater extent the acceleration of the dissociation of the β-ether linkages and increase the yield of guaiacol to a greater extent than does anthraquinone.[30] The degree of delignification of wood in the sulphate and sulphite methods of preparation of cellulose increases after the introduction into the solution of 0.005–0.025% of molybdenum in the form of molybdenum-containing compounds.[31]

New methods for the oxidative delignification of plant raw material in a medium containing sodium hydroxide or sodium carbonate are being developed: the oxygen-alkaline or oxygen-soda delignification.[29] They are based on the ability of wood lignin to be converted by oxidants into soluble compounds with rupture of lignocarbohydrate linkages. The cheapest and ecologically cleanest reagent for the oxidation of lignin is molecular oxygen. The oxidation of organic compounds by molecular oxygen constitutes a thoroughly investigated field of catalysis. The selection of catalysts for the process presents no difficulties.[32] Here it is important to protect cellulose from degradation. This requires the development of rational methods for the introduction of catalysts into the wood raw material, the use of inhibitors preventing the oxidation of cellulose, and the selection of optimum process conditions.

An example of the use of metal complex catalysts in the oxygen-alkaline delignification may be provided by the increase by a factor of 2–3 of the rate of delignification of wood in the presence of catalytic amounts of transition metal complexes of *o*-phenanthroline (0.1–0.3% of the mass of the absolutely dry wood). Such complexes are formed as a result of the interaction of *o*-phenanthroline with the variable-valence metals present in the reaction mixture.[33]

The catalytic activity of transition metal ions can change during the oxygen-alkaline delignification process as a consequence of the change in the composition of the reaction mixture. For this reason, the introduction of $MnCl_2$ in the initial stage accelerates the degradation of wood polysaccharides. On the other hand if manganese chloride is introduced in a subsequent stage, the yield of cellulose rises (by 0.8–4.1%) and the quality of its fibres improves.[34]

In the presence of hexacyanoferrate(II) ions and additives preventing the degradation of cellulose (alcohol, amines, ethers), the yield of cellulose as the product of the oxygen delignification of lignocellulose raw material in an aqueous medium at 65 °C and pH 10–14 increases.[35] Certain catalysts, for example, tungsten and molybdenum oxyanions, promote the delignification of wood by hydrogen peroxide. This process can be achieved under comparatively mild conditions. Thus the delignification of firwood chips in the presence of tungstic acid (2% of the weight of the absolutely dry wood) takes place at 95 °C.[36]

There are instances of the effective application of metal complex catalysts in the bleaching of cellulose, although their role is not always ultimately clear. The selectivity of the delignification of cellulose in acid–alkaline bleaching increases in the presence of molybdenum and tungsten complexes introduced in an amount of 0.001% of the weight of the fibre.[37] The maximum effect is obtained when these catalysts are used together with stabilisers such as urotropine, triethanolamine, and trisodium phosphate.

The Co^{2+} complex of a Schiff base (*N,N'*-bis-salicylidene-ethylenediamine) accelerates the delignification and bleaching of beechwood,[38] the efficiency of its action increasing with decrease in the basicity of the medium. In oxygen-alkaline bleaching, the high-molecular-weight component of lignin undergoes oxidative degradation to fragments which are soluble in the bleaching solution. An amount of the catalyst such that the cobalt content is 0.1% of the weight of the lignin is optimal. Bis(3-salicylideneaminopropyl)-amine cobalt is the most stable under the conditions of the oxygen-alkaline delignification of wood.[39]

The compounds of certain transition metals (for example, titanium and vanadium) accelerate the peroxide delignification and bleaching of lignocellulose materials, preventing at the same time the oxidative degradation of the cellulose component of the plant raw material.[40] In the presence of tungsten, molybdenum, and chromium ions, the quality of the cellulose obtained improves.[41]

Catalysts can exert a positive effect also on non-oxygen cellulose bleaching processes. Thus, in the catalysis by Cu^{2+} ions (0.1–0.3%) of the hypochlorite bleaching of natron cellulose, the activation energy for the reactions occurring diminishes.[42]

2. Preparation of cellulose derivatives

Catalytic processes are being applied on an increasing scale in the chemical modification of cellulose in order to synthesise a wide variety of its derivatives. The conversion into ethyl groups and other reactions of the OH groups of cellulose are achieved and graft copolymers are obtained with participation of catalysts of the acid–base type and metal complex systems.

The $Fe^{2+}-H_2O_2$ oxidation-reduction system in which Fe^{2+} ions are bound to the COOH groups of cellulose initiates the grafting to cellulose of various monomers—vinyl acetate, methyl-5-vinyl-tetrazole, and dimethyl(carboxymethyl) ammoniaethyl methacrylate bromide.[43,44] The mechanism of the formation of graft polymers using the $Fe^{2+}-H_2O_2$ system postulates the oxidation in the first stage of Fe^{2+} ions to Fe^{3+} by hydrogen peroxide.[45] The Fe^{3+} ions promote the development of oxidation processes in cellulose, a decrease in the degree of its polymerisation, a decrease in the number of COOH groups, and an appreciable accumulation of carbonyl groups. The bulk of the graft polymer is formed in the subsequent stage initiated by the $Fe^{2+}-H_2O_2-$reductant system. The carbonyl groups of cellulose, formed in the initial stage of the process, can play the role of the reductant. The additional introduction of reductants (for example, hydroxylamine or hydrazine) makes it possible to eliminate the development of degradative processes in the first stage of the copolymerisation.

When cellulose is treated with an alcohol–benzene solution of $KMnO_4$, Mn^{3+} complexes, bound strongly to cellulose, are produced.[46] The formation of C–O–Mn linkages weakens the carbon–oxygen bond, which leads to the appearance of unpaired electrons on the carbon atoms in the 1-, 2-, and 3-positions in the anhydroglucose unit of cellulose. The free radicals arising as a result of the presence of an unpaired electron on the C(2) and C(3) atoms are capable of initiating the grafting of various compounds at the C(1) atom—they initiate the block copolymerisation of these compounds.

Ce^{4+} ions catalyse the grafting to cellulose of acrylonitrile, styrene, vinyl fluoride, vinylidene fluoride, methyl methacrylate, ethyl

acrylate, acrylamide, and the styrene–methyl methacrylate mixture.[47–49] Methyl methacrylate is grafted to cellulose in the presence of vanadium(V) acetyl-acetonate.[50] The use of the V^{5+}–cellulose xanthate oxidation-reduction system makes it possible to achieve a continuous method for the preparation of modified viscose fibre containing simultaneously quaternary ammonium and carboxy-groups.[51]

There are data[52] concerning the preparation of graft copolymers of cellulose with acrylic acid and the grafting of 4-vinylpyridine to cellulose in the presence of Co^{3+} ions. In order to obtain cellulose derivatives with a grafted lactone, polymerisation catalysts, especially tetramethyltitanium, are used.[53] Oxycellulose with a high content of carboxy- and carbonyl groups has been obtained by the catalytic oxidation of cellulose in the presence of $RuCl_3$.[54] In an acid medium, the reaction takes place at a higher rate even at 20 °C without appreciable degradation of cellulose.

V. Preparation of synthetic fuels

1. Liquefaction of coal

The heterogeneous catalysts for the liquefaction of coal have now been investigated in greatest detail.[55] However, there are also fairly numerous examples of the effective employment of homogeneous metal complex catalytic systems for this purpose.

Two main aspects of the use of dissolved catalytic systems in carrying out such processes have been established. One of them is associated with the search for low-temperature dissolved catalysts. The other is based on the application of solutions of catalytically active compounds as precursors of catalysts formed as a consequence of the decomposition of the initial substances at temperatures above the threshold of their thermal stability. It is noteworthy that it is not always possible to draw a clear-cut boundary between these versions owing to the insufficient information about the state of the catalyst employed.

It has been suggested that dissolved rhodium complexes with phosphine or amine ligands [for example, $RhCl(PPh_3)_3$ and $Rh_2(HCOO)_2(bipy)Cl_2$] as well as catalytic systems consisting of rhodium salts and added triphenylphosphine be used for the hydrogenation of coal under mild conditions.[56] Dissolved catalytic systems, obtained by the reaction of $FeCl_3$ and $Ni(COOH)_2$ with organoaluminium compounds and treated with H_2, exhibit a high activity in coal hydrogenation processes.[57]

At 400 °C and a hydrogen pressure of 13.5 MPa, the degree of conversion of brown coal in the presence of the above catalysts is 90%. At an elevated temperature and pressure, a high degree of liquefaction of coal is attained in the presence of organocobalt complexes soluble in the reaction mixture.[58]

Cheap iron catalysts for the hydrogenation of coal are of greatest interest from the practical standpoint. The influence of the composition of iron compounds and of the methods for their introduction into coal on the liquid product formation processes has been investigated. The iron cations introduced into coal by ion exchange are not inferior in their catalytic activity to industrial aluminocobalt–molybdenum catalysts of the hydrogenation of brown coal.[59]

The reaction of coal with iron salts under the conditions of the synthesis of ferrocene affords iron compounds resistant to the action of acids and alkalis.[60] NMR and IR spectroscopic data, comparison of model substances, and analysis of literature data have made it possible to conclude that, on interaction with coal, iron forms π-complexes of the type of ferrocene.

There are data showing that the degree of conversion of brown coal at 450 °C increases in the presence of the ferrocene complex of iron and iron pentacarbonyl, acetate, acetylacetonate, and chloride.[61] The iron pentacarbonyl complex $Fe(CO)_5$ exhibits the highest activity.[62] Being liquid at the usual temperature, it mixes readily with organic solvents, penetrates deeply into the coal pores, and decomposes at 300 °C with formation of highly dispersed metallic iron. The catalytic effect of iron pentacarbonyl and also of molybdenum and tungsten carbonyls intensifies when they are used together with elemental sulphur. Under these conditions, highly dispersed particles of the metal sulphides are formed in the course of the reaction. They are more active in the liquefaction of coal than the metals themselves.

From the economic standpoint, it is preferable to use the $CO + H_2O$ mixture for the liquefaction of coal instead of the expensive H_2. This process can be accelerated by the oxyanions of certain transition metals.[63] In the course of the liquefaction of coal at 400 °C, the complexes of tungsten, molybdenum, chromium, and manganese in the highest oxidation states are reduced, forming compounds insoluble in water, which makes it possible to remove the catalytically active metal from the solution. It has been suggested that metal-carboxylic acids are formed in the presence of CO and then decompose to the metal hydride and CO_2. Metal hydrides reduce coal or react with H_2O, liberating H_2.

2. Liquefaction of the plant biomass

The high content of oxygen in the plant biomass makes it irrational to use H_2 in the liquefaction processes, since a large amount of it is consumed on the removal of oxygen in the form of H_2O. Nevertheless, there are examples of the use of heterogeneous and homogeneous catalysts in processes involving the hydrogenation of wood and its principal components by molecular hydrogen. Thus, in the presence of dissolved catalytic systems based on iron, molybdenum, cobalt, and copper compounds, the degree of conversion of cellulose reaches 93% at temperatures in the range 250–350 °C and an initial H_2 pressure of 5 MPa.[64] Mainly water-soluble organic compounds and gaseous products, among which CO and CO_2 predominate, are formed. Competing reactions involving the hydrolysis, pyrolysis, and hydrogenation of cellulose take place simultaneously. Pyrolysis predominates at 250 °C, hydrogenation begins to prevail on raising the temperature to 300 °C, and dehydrogenation and charring of the cellulose predominate at 350 °C. The best hydrogenation catalysts at all temperatures are molybdates. The minimum consumption of H_2 is achieved when chloride catalysts—$CuCl_2$ and $FeCl_3$—are used.

In the presence of solvents with H-donor properties, the wood raw material is liquefied without the participation of H_2. The use of compounds such as $CoCl_3$ and $CuCl_3$ as dissolved catalysts makes it possible to convert cellulose into products soluble in aqueous or aqueous-organic media.[65]

Catalytic biomass liquefaction processes in an aqueous medium on treatment with carbon monoxide and synthesis gas have been vigorously investigated in recent years. The use of CO, which is cheaper than hydrogen, makes it possible to trap the oxygen of the biomass in the form of CO_2. The catalytic effect when carbon monoxide is used as the reductant is achieved as a result of the formation of metal formates, which act as reductants. The virtually complete conversion of wood in water (up to 99% relative to the dry ash-free mass) can be attained by impregnating it with

$Fe(NO_3)_3.3H_2O$ or $Co(NO_3)_3.6H_2O$ solutions and by subsequent treatment at 350–420 °C under a pressure of synthesis gas of 10.5–36.4 MPa.[66] The yield of the liquid products is 75%. Nickel compounds can also serve as catalysts. Thus, when $NiCO_3$ is added to a suspension of wood filings in water, the degree of conversion of wood increases by a factor of 3.[67]

3. Thermochemical reactions of solid fuels

In the high-temperature catalytic pyrolysis and gasification of coal and biomass, metal complexes were used in the stage involving the formation of catalytically active surface compounds or highly dispersed particles of the active component.

The influence of catalysts on the yield and porous structure of wood charcoal in the pyrolysis of wood and its components has been investigated. The use of metal chlorides with acid properties, for example, $TiCl_4$, $CrCl_3$, and $FeCl_3$, increases the rate of pyrolysis of hemicelluloses and cellulose by a factor of 10, reduces the wood degradation temperature by 100–150 °C, and increases the yield of the charcoal by a factor of 1.5.[68,69] It has been suggested that catalysts of this type accelerate the dehydration reaction. The compounds formed, containing aldehyde groups, condense to high-molecular-weight substances, which lead ultimately to an increased yield of wood charcoal.

Definite information about the processes occurring in the catalytic pyrolysis of wood is provided by the study of the thermal reactions of metal-containing celluloses.[70] The active role of molybdenum ions in the condensation reactions of partly degraded cellulose fragments is indicated by the results obtained when molybdenum-containing cellulose hydrate is exposed to high temperatures. During the pyrolysis of the iron-containing cellulose, the carboxylate ions are initially decarboxylated with the simultaneous reduction of Fe^{2+} cations to the metal. In the next stage, highly dispersed iron inclusions are oxidised to Fe_2O_3, which is accompanied by a significant loss of organic mass.

Catalytic pyrolysis can be used to obtain metal-containing carbon sorbents. During the pyrolysis of wood impregnated with iron, cobalt, nickel, and copper compounds, sorbents are formed with a porous carbon structure in which metallic particles are inserted.[71] On thermal decomposition of monocarboxycellulose substituted by Fe^{3+} cations, highly dispersed oxides seemingly retaining the lattice of the initial fibre, are formed.[72]

The conversion of the solid carbonaceous raw material into gaseous products of different composition takes place when it is subjected to a heat treatment in oxygen, water vapour, carbon dioxide, or hydrogen. The effect of certain catalysts makes it possible to accelerate the gasification process or to reduce its temperature while retaining a higher rate and, what is no less important, to regulate the composition of the gas formed.

In order to introduce catalysts into wood charcoal, the reactive groups of wood were subjected to ion exchange for metal compounds, after which the modified wood was subjected to pyrolysis.[73] The catalysts for the gasification of wood charcoal by carbon dioxide at 800 °C can be arranged in the following sequence in terms of their activities:

$$Co > Ca > Ni > Mg \sim K \sim Na > Cu.$$

The ion-exchange cobalt catalyst exhibits a very high activity. For example, wood charcoal is fully gasified by CO_2 at 600 °C after only 5 min.

Surface transition metal complexes play an important role in the catalytic gasification of solid fuel. Technical carbon, carbon fibre, and graphite containing titanium, vanadium, and chromium surface compounds of the C–O–M type were used as model objects in one of the studies.[74] The grafting of the transition metal complexes to the surface of the solid material makes it possible to increase by two orders of magnitude the rate of gasification and to lower the temperature and activation energy for the reaction.

In order to investigate the activities of iron catalysts in processes involving the gasification of carbonaceous materials by steam and hydrogen, iron compounds were introduced into a carbon support by impregnating the latter with the corresponding aqueous solutions or by means of ion exchange. It is suggested that in the course of the reaction the surface metal complexes are reduced, forming highly dispersed species which effectively catalyse the gasification process at temperatures above 700 °C.[75]

When two-component catalytic systems, including a transition and an alkali metal, are used for the gasification of carbonaceous materials, synergistic effects are observed. In processes involving the gasification of coal by steam at 700–800 °C, the maximum activity is shown by the $Na[HFe(CO)_4]$ and mixed $Fe(NO_3)_3 + Na_2CO_3$ systems.[76] Sodium hydrotetracarbonylferrate accelerates the gasification of coal by steam at 700 °C by a factor of 4.5.[77] For comparison, we may note that an increase in the rate of the non-catalytic gasification by a factor of 6 requires an increase in temperature from 700 to 1000 °C.

The observed non-additive increase in the activity of the mixed system has been explained by the fact that alkali metals facilitate the stage in which iron oxides are reduced by carbon, which limits the rate of the process as a whole. There are data showing that iron and nickel acetylacetonate complexes behave as process catalysts, while K_2CO_3 increases the surface area of the carbonaceous material in the gasification process.[78]

A specific feature of the gasification of solid fuels is that under the reaction conditions carbon is not only one of the reactants but also serves as the carrier for the catalyst. There are data indicating the formation of intercalation compounds of the metal during heat treatment at elevated temperatures.[79] It has been suggested[80] that metal–carbon inclusion complexes can play the role of catalytic centres in the gasification reactions. At the beginning they are not accessible to the gasifying agent but are involved in the process to the maximum extent for a degree of conversion of carbon up to 80%. The formation of metal–carbon complexes also prevents the vaporisation of the deposited metal compounds during heat treatment; they become active after the burning away of an appreciable proportion of the carbonaceous material. It is entirely possible that the mechanism of the catalytic gasification of the biomass includes as the main stages the interaction of the metal-catalyst cation with the surface phenolic, alcoholic, and acid groups of the organic matrix and the subsequent thermal decomposition of the resulting surface metal complexes.[81]

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Metal-complex catalysis of the polymerisation of α-olefins

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ABSTRACT. The progress in the development and application of metal-complex catalysis in the polymerisation of α-olefins during the last ten years is reviewed and evaluated. The methods of modifying previously known catalytic systems are characterised and the experimental results of studies on novel types of catalysts, including Ti–Mg, metallocene, lanthanide, and ylide systems are reported. Some views about further improvement of the activity and stereospecificity of metal-complex catalysts in relation to the chemistry of polyolefins are stated.

The bibliography includes 242 references.

Contents

I.	Introduction	1193
II.	Modification of classical Ziegler–Natta catalytic systems	1194
III.	Novel types of catalytic systems	1196
IV.	Emergence of new possibilities for developing highly active metal-complex catalytic systems	1202

I. Introduction

An event which caused a revolution in chemistry in this century was the discovery by K Ziegler and G Natta of the metal-complex catalysis of the polymerisation of olefins. This discovery was not only of outstanding scientific importance but also gave rise to a fundamentally new and simple method of obtaining one of the most important industrial polymers — polyethylene — and to the synthesis of previously unknown crystalline stereoregular polyolefins such as polypropylene and several others. It is perhaps difficult these days to find an area of chemistry that has not experienced in its theoretical and practical aspects the influence of metal-complex catalysis to a greater or lesser extent. Metal-complex catalysis has had a considerable effect on the devlopment and refinement of the priority areas of theoretical and applied chemistry such as the polymerisation of dienes and the production of stereoregular rubbers, the activation of alkanes, highly effective and selective processes for the hydrogenation of unsaturated compounds, hydroformylation, and many others.

It has gained firmly established positions in the present-day chemical industry both in the production of large-tonnage products which govern the industrial potential of a country and in the preparation of products of so-called fine chemistry. Note the final role is also played by metal-complex catalysis in the development of certain biotechnological processes, the significance of which has grown in recent years.

However, the most important area of application of metal-complex catalysis (MCC) in industry still remains the polymerisation of unsaturated hydrocarbons — α-olefins, dienes, acetylenes, and, for the time being to a lesser extent, allenes.

A metal-complex catalytic system used for the polymerisation of α-olefins consists of three main components: 1) a transition metal; 2) a ligand (or several different ligands) bound to the transition metal); and 3) an electron-donor and/or electron-acceptor compound which has a direct effect on the activity and selectivity of the whole system, including the stereoselectivity (in the polymerisation of C_3 olefins or higher). Moreover, if a heterogeneous metal-complex catalyst is used, it contains a polymeric or other type of support as a matrix, the nature of which also affects the stability, selectivity, and activity of the whole catalytic system.

A virtually unlimited number of catalytic systems can be produced by varying the types of components as mentioned above. And in fact, since the discovery and application of Ziegler–Natta metal-complex catalysts, many hundreds if not thousands of catalytic systems for the polymerisation of ethylene, the stereospecific polymerisation of α-olefins (C_3–C_6), dienes, and acetylenic and allenic hydrocarbons have been proposed and in the majority of cases patented. However, until recently only certain compounds of transition metals such as Ti, V, and Cr have found practical application. Many fundamental studies and practical developments have been devoted to metal-complex systems based on them.

There is now no doubt that a necessary condition for catalysis to take place is the coordination of substrate (this is the monomer in polymerisation reactions) with a transition metal compound. The resulting organometallic intermediates participate in the polymerisation process, govern its mechanism, and have a considerable effect on the reaction kinetics and structure of the polymer formed.

However, up to the present time the nature of the active sites and the means of regulating their action have remained in many respects uncertain.

The composition of the intermediates depends on the nature of the transition metal in the catalytic complex, the type of ligand environment, and the donor-acceptor interactions that occur in the reaction sphere. All of these factors cause complications in making a reliable determination of the structure and mechanism of the active sites, which at the present time is made even more difficult because of the widespread use of metal-complex systems immobilised on a polymeric (or other) matrix, since in this case the actual structure of the active site may be considerably modified.

In the development of a metal-complex catalyst it is necessary to aim for a suitable combination of effectiveness, stability, and stereoselectivity. Many groups of researchers are working on a solution to these problems.

This is usually achieved through modification of classical Ziegler–Natta catalytic systems or through the development of new types of catalytic systems.

There is a whole series of theoretical and experimental publications and reviews in the Soviet and foreign literature on this topic.[1–22] Despite this, the problems of MCC in the polymerisation are still a long way from a complete solution and they leave open a sufficiently wide field for scientific research and advances. This has been the reason for writing the present review.

II. Modification of classical Ziegler–Natta catalytic systems

Bearing in mind the undoubtedly provisional nature of the classification that we have adopted, we shall classify catalytic systems made up by compounds of Ti, V, Cr, and certain other transition metals in combination with Al alkyl derivatives as classical Ziegler–Natta systems. The greatest number of studies are devoted to Ti-containing catalytic systems, which were discovered and first studied by Ziegler and Natta et al.[2]

In the polymerisation of ethylene and other α-olefins with catalysts containing Ti compounds, the high activity of the Ti–C bond is of considerable importance. This activity is related to its low energy and the possibility of selective excitation by insertion of a polymerising monomer.[23,24]

In a number of fundamental studies by Soviet research workers who had studied the properties of the Ti–C bond in quite considerable detail, a theory concerning the "lability" of this bond was advanced. The concept of "lability" denotes that the energy profile of the titanium-carbon bond (and in the final analysis its energy) is highly sensitive towards the ligand environment of the metal and towards association and dissociation, protonation and complexation.[8]

Some experimental results indicate the possibility of activation of the Ti–C bond, and hence an increase in activity of the whole catalytic system in the polymerisation of olefins. Thus, it was shown[24–32] that the activation of the metal-carbon bond (through to its homolytic decomposition) occurs on treatment of organic bases, Lewis acids, proton-donating compounds, and also microquantities of water.

The form of the titanium-containing components used in metal-complex systems has a considerable effect on the activity and stereoregularity of polymerisation (in the case of propylene polymerisation).[33–43] Thus, by using microspherical $TiCl_3$ it is possible to achieve a 98% (or higher) degree of isotacticity of the resulting polypropylene.[44–47] It is also significant that microspherical $TiCl_3$ makes it possible directly to obtain granulated polypropylene, which cannot be produced using traditional Ziegler–Natta catalytic systems, and hence an energy-consuming stage—granulation of the polymer—can be eliminated in the production of polypropylene. The structure (sphere) of the catalyst is replicated, as it were, in the polymer.[37]

Improvement of the classical catalytic system $TiCl_3 + AlR_3$ has mainly proceeded in the direction of the introducing certain activating additives, amongst which organomagnesium compounds are of the greatest interest.[48–51] Catalysts modified with these additives constituted the prototype of novel Ti–Mg metal-complex systems that will be examined below.

Table 1[52] contains the experimental results that characterise the activity of modified catalysts for the polymerisation of ethylene. For comparison we can indicate that on typical Ziegler–Natta systems the yield of polyethylene per unit of catalyst is lower by a factor of about 1.5–2.

Table 1. Activity of Ti–Al ethylene polymerisation catalysts modified with organomagnesium compounds.

Components of the catalytic system			Output g PE (g Ti)$^{-1}$	[η], dl g^{-1}
Ti	Al	Mg		
$TiCl_4$	$(C_2H_5)_3Al_2Cl_3$	$(C_6H_5)_2Mg$	18 420	13.8
	$(C_2H_5)_2Al_2Cl_4$	$(C_6H_5)_2Mg$	19 300	13.0
	$(C_2H_5)_3Al$	$(C_6H_5)_2Mg$	31 600	11.2
	$(C_4H_9)_3Al$	$(C_6H_5)_2Mg$	21 140	12.3
	$(C_2H_5)_x(C_4H_9)_yAl$	$(C_6H_5)_2Mg$	18 380	14.2
	$(C_2H_5)_2AlCl$	**$(t\text{-}C_4H_9)Mg$**	18 375	18.6
	$(C_2H_5)_2AlCl$	**$(n\text{-}C_3H_7)_2Mg$**	32 700	16.2
	$(C_2H_5)_2AlCl$	**$(n\text{-}C_4H_9)(OC_3H_7)Mg$**	24 500	17.2
	$(C_2H_5)_2AlCl$	$C_{12}H_{25}MgBr$	34 160	19.9
$Ti(OC_4H_9)_4$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	20 120	22.6
$Ti(OC_4H_9)_3Cl$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	21 000	20.8
$Ti(OC_4H_9)_2Cl_2$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	22 400	24.1
$Ti(OC_4H_9)Cl_3$	$(C_2H_5)_2AlCl$	$(C_6H_5)_2Mg$	20 800	23.8

It had already been established in the earliest studies on the polymerisation of ethylene on Ziegler–Natta catalysts that the molecular weight of polyethylene can be controlled by adding hydrogen, which terminates the chain.[53–56] However, it was shown recently that in certain cases hydrogen can at the same time increase the activity of the catalyst.[55] At the present time the mechanism of this phenomenon is the subject of study and so far there is no unequivocal view about the activating role of hydrogen.

The activating effect of hydrogen on metal-complex catalysis was observed not only in the polymerisation of ethylene but also that of propylene and other α-olefins.[57–59]

Microspherical $TiCl_3$ has also been successfully used for the copolymerisation of propylene and styrene.[60] The best results were achieved when the catalytic system $(RC_5H_4)_2TiMe_2$ (R = H, Me_3) + $TiCl_3$ was used. It is possible to obtain statistical copolymers of styrene and propylene by using this catalyst. When it is used, highly isotactic polymers based on propylene (isotacticity >99%), n-butene (isotacticity >98%), and polystyrene (isotacticity >99%) are obtained. For the polymerisation of ethylene highly crystalline polyethylene was formed, containing virtually no ethyl branches in the macromolecule.[44,45]

Block copolymers of propylene and ethylene were synthesised using microspherical $TiCl_3$.[61,62] In order to improve the morphology of the copolymer of ethylene and propylene obtained using δ-$TiCl_3/Al(C_2H_5)_3$, it is recommended to carry out a preliminary activation of this catalyst with small quantities of α-olefins (C_4–C_{12}) or ethylene.[63] Certain attempts were made to define the role of this process.[56,64–66] However, this phenomenon requires a more detailed investigation.

As has been mentioned above, donor-acceptor interactions which occur when electron-donating or electron-withdrawing compounds are added to the reaction sphere have a significant effect on the

activity of Ziegler–Natta catalysts. A large number of examples attesting to this effect have been reported in the literature.[67–73]

The recently published results of Seppälä and Härkönen,[74] who studied the polymerisation of propylene on Ziegler–Natta catalysts incorporating organosilicon donor components, have attracted attention. The following silicon compounds were used as donor additives: $RSi(OCH_3)_3$, $R^1R^2Si(OCH_3)_2$, $RSi(OC_2H_5)_3$, $R^1R^2Si.(OC_2H_5)_2$, $RSi(CH_3)_3$, $R_2^1R^2SiH$, $(n\text{-}C_3H_7O)_3SiCH_3$, $(CH_3)_2Si.[OC(CH_3)=CH_2]_2$.

It was established that the donor components in essence selectively deactivate the atactic active sites, thus increasing the yield of high-molecular weight isotactic polypropylene. The study contains data that characterise the relationship beween the effect of the above donors and their structure.

Interesting results were recently published by Soga et al.,[75] who proposed the use of spherical $TiCl_3$ in combination with Cp_2TiMe_2 without involving organoaluminium compounds in the catalytic complex for the preparation of isotactic polyolefins from propylene, 1-butene, and 4-methyl-1-pentene.

One of the most important methods of modifying Ziegler–Natta catalytic systems is their heterogenisation or, in other words, the immobilisation of the active sites on a support. Inorganic compounds as well as polymers themselves—polyethylene, polypropylene, etc.—can be used as the supports. Immobilised metal-complex systems have considerably greater stability compared to conventional systems and also prove to be more efficient in carrying out polymerisation under industrial conditions.[1,19,76–90]

Amongst the first to start work in this area were Kabanov et al.,[91–92] who developed the so-called gel-immobilised catalytic systems (GCS). In order to obtain such catalysts, functional monomers are initially grafted on to the polymers, for example, a functional monomer such as vinylpyridine or some other is introduced on to butadiene-styrene rubber by copolymerisation (normal or block), and then transition metal compounds [$TiCl_4$, VCl_4, Cp_2TiCl_2, $Ti(OPr)_4$, etc.] are added to the solvent-swollen rubber (gel), fixing on to the functional groups. After removal of the solvent the gel-immobilised catalyst (GC) can be kept in air, not losing its potential activity over a long period. When a GC is introduced into a solvent in which the polymerisation of ethylene or another α-olefin is being carried out it swells and the active sites become accessible for interaction with the monomer and the usual co-catalysts—AlR_2Cl, AlR_3, etc. It should be noted that in those cases where the rate of polymerisation exceeds the rate of diffusion processes related to removal of polymer from the gel, it is possible to destroy the whole system. Therefore, the use of GCS proves to be most effective in processes involving oligomerisation of olefins.

The functionalisation of polyolefins for the successive fixing of transition metal compounds on to them via suitable functional groups has been carried out.[26] Thus, Ti-containing catalysts for the polymerisation of propylene that were immobilised on polypropylene via acrylate groups were obtained, having high stability and making it possible to prepare isotactic polypropylene (96–97%).

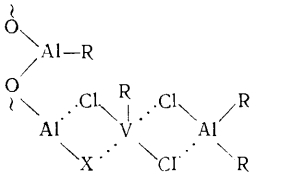
Recently the heterogenisation of homogeneous metal-complex catalytic systems was carried out by means of chelation with macroligands.[93] In order to do this, the functionalisation of the surface of PE was initially carried out. The functionalised support was then transformed through polymer-like reactions into chelating macroligands which formed a heterogenised catalyst with transition metal compounds. The transition metal compounds used were $TiCl_4$, $Ti(OC_4H_9)_4$, VCl_4, $Ni(OCOCH_3)_2$, $CoCl_2$, and $Co(OCOCH_3)_2$.

The bifunctional immobilised catalyst containing Ni and Ti (or V) compounds that is used for the single-stage preparation of linear low-density polyethylene (LLDPE) deserves particular attention. Its action is based on the effective dimerising ability of the Ni-active sites. Ti or V compounds traditionally used in Ziegler–Natta catalysts constitute the second active site in this catalyst.[93]

There is no doubt that the idea of obtaining LLDPE from ethylene in a single stage is attractive, but it is necessary to bear in mind the complexity of controlling simultaneously the different active sites that are functioning.

Attention has been drawn in the literature to the nature of the active sites of supported vanadium catalysts for the polymerisation of ethylene. For immobilisation of the components of the catalyst, supports that contained hydroxyl functional groups (and adsorbed water)—$SiO_2.Al_2O_3.H_2O$, kaolin, chalk, pyrite—and also supports with reactive alkyl groups—polyalkylalumoxanes $R_2Al(OAlR)_m-(OAlX)_m-OAlR_2.kEt_2O$, where X = Cl, OMg, iso-Bu, $OR(OC_6H_5)_2$; $n + m \geqslant 20$; $k = 0.1$—were chosen.[94–96] The higher valency vanadium compounds used were $VOCl_3$, VCl_4, $VO(OEt)_3$, and ethyl and isobutyl derivatives of aluminium were used as the organoaluminium component.

Si–O–V and V–O–Al bonds were fixed on the surface of the support. $Al(iso\text{-}Bu)_3$ served as the co-catalyst. It was shown experimentally that in catalytic complexes of supported systems chemical bonding of vanadium to the surface of the support occurs, lowering the mobility of the vanadium atom and reducing the probability of octahedrally coordinated vanadium being formed. The highest catalytic activity in the polymerisation of ethylene occurs in vanadium-alumoxane systems in which the active site is not bound chemically to the support. The structure of the active sites of vanadium alumoxane catalysts can be represented schematically as follows:



,

X = R, OR, Cl, OMgR, OP $(OC_6H_5)_2$.

The vanadium catalysts immobilised on alumoxanes are more stable than those immobilised on oxide supports. Their output is also higher by a factor of 4–6.

In one study[97] several new approaches to stereoregulation processes in the polymerisation of propylene on solid complex catalysts based on α- and δ-$TiCl_3$ (or VCl_3) + AlR_3 (or AlR_2Cl) were examined. The mechanism of polymerisation was shown to be multicentred. The active sites of the catalyst differed according to both reactivity and stereoregulating ability.[98]

It is significant that an isotactic fraction of PP that has virtually uniform stereoregularity is not of uniform molecular weight. This fact suggests that the two types of active site in the catalyst are not interrelated in terms of activity and stereospecificity. It is necessary to take into account this factor when interpreting the experimental data on the stereospecific polymerisation of propylene and other α-olefins.

Soviet research workers[99] studied the mechanism of the formation and structure of the active sites formed when organometallic catalysts are fixed to the surface of a support. This is of considerable importance for achieving controlled polymerisation of ethylene and other α-olefins on heterogenised catalysts, since the

process of fixation of the active sites on the surface of the support and the subsequent polymerisation are accompanied by a number of quite complex side reactions that have an effect on the activity of the whole catalytic system and the kinetic mechanisms of polymerisation. The fixation of metal complexes of $TiCl_4$ and $AlEt_2Cl$ or $AlEt_3$ to the surface of Aerosil was selected as a model.

It was established that in the polymerisation of ethylene and propylene on this catalytic system, different types of active site can occur depending on the conditions under which it is formed. Thus, when a titanium compound that is already fixed is treated with organoaluminium compounds (the "direct" method), titanium occurs on the surface of the support as a separate $TiCl_4$ complex, and a $TiCl_3$ phase is not formed, as was previously supposed.[82]

The use of the "reverse" method for fixing the catalyst, in which $AlEt_3$ is fixed first, results in the formation of a $TiCl_3$ phase on the surface of the support. When $AlEt_3$ interacts with the OH groups of Aerosil, alkyls of the type $Si-O-AlEt_2$ are formed on the surface, having good reducing ability. According to polarographic data, after interaction of such groups with $TiCl_4$ a system containing a maximum quantity of Ti^{3+} (95%) and containing virtually no Ti^{4+} or Ti^{2+} is formed.

If $AlEt_2Cl$ is used instead of $AlEt_3$, the active sites formed on the surface in the "reverse" method of producing fixed metal complexes are quite different in nature. In this case reaction with OH groups results in the formation of $Si-O-Al$ compounds of lower reactivity, and after adsorption of $TiCl_4$ a surface complex is formed in which titanium remains almost completely in the tetravalent state. Such sites are highly active in the polymerisation of propylene, as a result of which irregular low-molecular weight polypropylene is formed.

According to IR spectroscopy data the polypropylene formed on sites of this type contains a large number of irregular additions and is similar to the polypropylene obtained on classical cation catalysts (BF_3, $AlBr_3$). The atactic fraction of polypropylene is virtually no different from the traditional form.

Thus from the experimental data examined above it can be concluded that there is a possibility of the directed formation of different active sites in the polymerisation of α-olefins on heterogenised Ziegler–Natta catalytic systems.

In two studies by D'yachovskii et al.[100,101] it was found that when catalytic systems based on $Ti(OR)_4$, $TiCl_3$, and $VO(OR)_4$ fixed on graphite were used, it was possible to obtain highly isotactic PP. The theory was advanced that the graphic acts as a unique macroligand that permits the formation of active sites with a high stereoregulating capacity.[101,102] The graphite support was also successfully used in the polymerisation of 1-butene on Ziegler–Natta catalytic systems.[103]

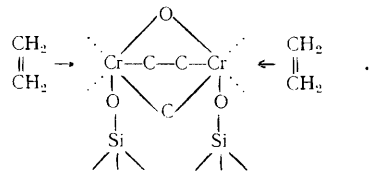
There is no doubt that the role of a graphite support, which has unusual properties that other layered supports may also possibly have, deserves detailed study. This opens up new possibilities for the development of unconventional heterogenised metal-complex polymerisation systems.

X-Ray diffraction studies were carried out[103] on the polymerisation of 1-butene on Ziegler–Natta systems fixed on graphite and they helped to identify the properties of the graphite support with a number of transition metal compounds ($TiCl_4$, $SnCl_4$, $FeCl_3$, etc.) fixed on it. The X-ray diffraction studies demonstrated that these complexes penetrate inside the quasi-monocrystalline graphite. However, the distance between the carbon layers in the graphite when it is treated with heptane, $AlEt_2Cl$, $TiCl_4$ + $AlEt_2Cl$ does not alter, namely, the formation of layered graphite compounds does not occur with these products.

As a result of the polymerisation of ethylene and 1-butene in the presence of the catalytic system $TiCl_4$ + $AlEt_2Cl$ fixed on a quasi-monocrystal of graphite, the crystal expands and increases its width by a factor of 3–5 depending on the polymerisation conditions. This suggests that the polymerisation of olefins occurs both on the outer surface and inside the crystal. Thus, the hypothetical concept which regards graphite as a macroligand requires experimental confirmation.

At the same time as Ziegler–Natta catalytic systems, chromium oxide catalysts comprising Cr compounds deposited on Al_2O_3 (Phillips catalysts) were proposed and even found industrial application for the polymerisation of ethylene.[2,104,105] In due course the characteristics of the polymerisation of ethylene and other olefins on these catalysts were studied in detail by Topchiev et al.[106] and the chemical interaction between transition metal and support was demonstrated experimentally. The interest in chromium oxide catalysts has now diminished somewhat because of the development of new highly effective and stereoselective catalytic systems. Nevertheless, several studies have appeared in the literature in recent years[107–111] devoted to chromium catalysts for the polymerisation of ethylene.

Thus, in a recently published study by Rebentorf[112] the number of active sites in samples of a Phillips catalyst—0.5% Cr^{6+} and 0.074% Cr^{6+} (on silica gel)—was determined. It was shown that the number of active sites increases with a decrease in Cr content in the catalytic system. Rebentorf, in the same way as the Soviet scientists, assumes that in this case there is chemical reaction between Cr and the support:[112]



Gan et al.[108–110] examine a new type of chromium catalyst for the polymerisation of olefins, consisting of specially prepared chromium acetate combined with $AlEt_2Cl$. This catalyst exhibits a very high activity in the polymerisation of ethylene, amounting to 1180 g PE (g Cr)$^{-1}$ h^{-1}.

III. Novel types of catalytic systems

1. Titano-magnesium catalytic systems

In considering the different methods for modifying "classical" Ziegler–Natta catalytic systems we have already drawn attention to the activating effect of organomagnesium compounds. These studies have served as the basis for the development of a new generation of highly active Ti–Mg catalysts. At the present time heterogeneous titano-magnesium catalysts represent the most widely used metal-complex systems for the production of polyethylene and other polyolefins, in particular, isotactic polypropylene. Essentially these catalytic systems are supported, since $MgCl_2$ should legitimately be regarded as a support. Experimental data characterising the activity and stereospecificity of certain titanomagnesium catalysts used in the polymerisation of propylene are presented in Table 2.[113] It should be noted that in all cases the fairly high stereospecificity of such catalysts is due to the addition of electron-donating compounds (ethers and esters, phosphorus- and silicon-containing compounds, etc.).

Ti–Mg catalysts (in their various forms) have served as a subject of research for scientists of different countries.[1,114–123] A considerable contribution has also been made to the development and practical application of Ti–Mg catalysts by Soviet scientists (the school of Yu E Ermarkov and V A Zakharov in the Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences).[82,120,124–128]

Table 2. Some results on the polymerisation of propylene on titanium–magnesium catalysts.[113]

Solid catalyst	Co-catalyst	Activity, g PP (g Ti)$^{-1}$	Index of isotacticity
$TiCl_3$	$(MeC_5H_4)_2TiMe_2$	27	98
	$(MeC_5H_4)_2TiCH_2(Me)AlMe_2$	37	93
$TiCl_4/MgCl_2$	$(MeC_5H_4)_2TiMe_2$	160	90
	$Cp_2TiCH_2(Me)AlMe_2$	940	87
$TiCl_4$/EB*/$MgCl_2$	Cp_2TiMe_2	970	95
	$Cp_2TiCH_2(Me)AlMe_2$	3250	93
$TiCl_4$/n-BP**/$Mg(OEt)_2$	Cp_2TiMe_2	60	97
	$Cp_2TiCH_2(Me)AlMe_2$	2400	97
$TiCl_4$/n-BP/$MgCl_2$	Cp_2TiMe_2	90	96
	$Cp_2TiCH_2(Me)AlMe_2$	3700	95
	$AlEt_3$	4000	76

Polymerisation conditions: $P_{C_3H_6}$ = 1 atm, T = 40 °C, τ = 2 h, heptane solvent (100 ml).

* EB = ethyl benzoate. **n-BP = n-butyl phthalate.

Attention is drawn in the literature to the fact that the properties of Ti–Mg catalysts depend to a significant extent on the structure of the support and the method of fixing transition metal compounds to it. Magnesium chloride is the most suitable support for obtaining a highly active propylene polymerisation catalyst because of the similarity between the structures of $TiCl_3$ and $MgCl_2$.[129–134] Thus, an active catalyst was obtained by grinding together a mixture of anhydrous $MgCl_2$ and the complex $TiCl_4.C_6H_5-COO-C_2H_5$. The ester is an electron donor and it is needed to achieve a high degree of stereoregularity. On a catalyst prepared in this manner the yield of PP reached 9 to 17 kg (g M)$^{-1}$ h^{-1} with a degree of isotacticity of 94–95%.[135]

Polish research workers[135] showed that the presence of a given quantity of ethanol in the reaction medium during preparation of the catalyst increases the efficiency of a Ti–Mg catalyst (modified none the less with ester). During the experiment the presence of ethanol assisted the formation of the spherical type of catalyst grain. However, the specific output of the catalyst was not sufficiently high ~6 kg PP (g Ti)$^{-1}$ h^{-1}.[135]

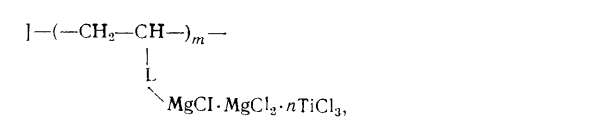
A detailed study was made on the copolymerisation of ethylene with α-olefins on Ti–Mg and similar supported catalytic systems. The subject of the study was the suspension copolymerisation of ethylene with propylene, 1-butene, and 1-hexene on supported Ti–Mg (TMC) and V–Mg (VMC) catalysts.[111] In the copolymerisation on TMC and VMC the catalysts can be arranged in the following order of copolymerising ability: V–Mg > $TiCl_3$ > Ti–Mg. It was established in a separate series of experiments that there is a virtually constant value of the copolymerisation constant over the temperature range 40 to 80 °C.

As has already been mentioned above, the structure of the electron-donating component has a significant effect on the activity and stereospecificity of Ti–Mg catalysts.[136–145] In this respect consideration should be given to a recently published study,[146] in which a new highly active supported catalyst for the polymerisation of propylene based on $TiCl_4$ and $MgAlk_2$ compounds and sterically hindered aromatic esters is described, the esters used being ethyl 2,6-dimethylbenzoate, ethyl 2,4,6-trimethylbenzoate, or isopropyl benzoate. The support is deposited from a solution of $MgAlk_2$ with SiR_4 and then activated by treatment with $TiCl_4$ and dibutyl phthalate in chlorobenzene. A Ti–Mg catalyst prepared in this manner gives high yields of isotactic PP [16–17 kg PP (g Ti)$^{-1}$ h^{-1}] (70 °C, 10 atm).

There are reports in the patent literature[147–152] on many methods for preparing Ti–Mg catalysts which we naturally do not have the opportunity of examining within the scope of this review. A number of studies[31,122,140,142,153–175] are devoted to establishing the nature of the active sites of Ti–Mg catalysts.

The desire to increase the number of isospecific sites in a Ti–Mg catalyst has compelled research workers to seek the most effective electron-donating components which cause an increase in the number of these same active sites. Amongst the electron-donating components studied, special consideration should be given phthalate esters.[142–144] In a study of the copolymerisation of ethylene and 1-hexene, 1-decene, and 4-methyl-1-pentene on a Ti–Mg catalyst, Ivanchev et al.[176,177] and also other research workers[56,63–65,178] showed that the α-olefin molecules act as modifiers of the growth sites, increasing the rate of growth of the polymer chain by a factor of 6–9. This interaction during the suspension polymerisation process is satisfactorily represented by a scheme involving equimolar equilibrium complexation with a constant that is close to unity.

Interesting results were obtained by Krentsel' et al.[8] in a study of the polymerisation of ethylene on Ti–Mg catalysts that were immobilised on polymeric supports. The structure of the catalyst used in this study can be represented by the following general scheme:



where L is a functional group such as allyl alcohol, acrylic acid, and others. The steady-state rate of ethylene polymerisation at 70 °C and 2 atm reached 85 mol C_2H_4 (mol Ti)$^{-1}$ s^{-1}.

This type of Ti–Mg catalyst for the polymerisation of ethylene is characterised by a low Mg content which is comparable to the concentration of Ti, which, in the opinion of Krentsel' et al.,[8] makes it possible to control the molecular weight properties of polyethylene.

In general, control of the molecular weight and molecular weight distribution of polyethylene formed by the polymerisation of ethylene on Ti–Mg catalysts is a complex task. In this respect the studies which demonstrated the possibility of controlling the molecular weight distribution in the polymerisation of ethylene on Ti–Mg catalysts by the introduction of various halogenated compounds such as butyl chloride, chlorobenzene, and others are of undoubted interest.[179,180] From the experimental data obtained it

could be assumed that termination of the chain occurred as a result of the addition of a strongly polarised RX molecule or contact ion pair R^+X^-. In all of the experiments there was a narrowing of the molecular weight distribution. However, for the time being it is not possible to provide a reliable explanation for this phenomenon. The mechanism of interaction between RX and an active site is so far unclear and requires further study.

It may be assumed that there is a certain critical size of the catalyst macroparticles, depending on which the process occurs in the kinetic or diffusion region. In turn this critical size depends on the activity of the catalyst sample used, being determined by the concentration of active sites and the rate constant of growth.

From an analysis of the experimental data on the polymerisation of ethylene and other α-olefins on supported Ti–Mg catalytic systems, these catalysts can be considered to be amongst those with the greatest future potential.

2. New homogeneous metallocene catalytic systems

The most prominent event in metal-complex catalysis of the polymerisation of α-olefins since the discovery of this reaction by Ziegler and Natta was the creation by Kaminsky et al. (FRG)[181,182] of new homogeneous catalytic systems based on metallocene-alumoxane complexes. Such catalysts, having very high activity in the polymerisation of ethylene (tens of tons of polymer per gram of metal) can be used to effect stereocontrol of polymers in a homogeneous reaction medium.[183] The considerable scientific and practical interest shown at the present time in all countries in such metal-complex systems is due to this factor.

Catalysts of this type are formed by reaction of a metallocene of a transition metal such as Zr, Hf, and others, for example, bis-(cyclopentadienyl)dimethyl(or dichloro)zirconium with alumoxanes

$$-\left(-\underset{\displaystyle R}{\underset{|}{Al}}-O-\right)_n-,$$

where R = CH_3, C_2H_5, etc., n = 10–20.

During the last few years a large number of studies devoted to the polymerisation of olefins on such homogeneous complexes, in particular on zirconocene complexes with alumoxanes have been published.[178,184–202] Experimental data characterising the relative activity of such homogeneous catalysts in the polymerisation of ethylene[189] are given in Table 3.

It was calculated for the zirconium catalyst that at a polymerisation temperature of −20 °C about 70% of all zirconium atoms participate in polymerisation.

Experimental data on the polymerisation of ethylene on different Zr-containing catalytic systems[189] are given in Table 4.

Homogeneous zirconocene catalysts proved to be active not only in the polymerisation of ethylene but also in the copolymerisation of ethylene with hexene. The latter process is of considerable practical importance and is used to obtain linear low-density polyethylene (LLDPE). This polyethylene differs from low density polyethylene obtained by high-pressure radical polymerisation in its lower degree of chain branching and improved mechanical properties.

Interesting results were obtained when organozirconium compounds complexed with oligomeric alumoxanes were used as ethylene polymerisation catalysts. These catalysts are distinguished by their stability and can be used to obtain PE with a narrow molecular weight distribution. Isotactic polypropylene with a novel steroblock microstructure was obtained by using soluble bis(cyclopentadienyl)bis(phenyl)titanium/methylalumoxane catalysts.[6]

Three reports[183,192,196] indicate the unusual effects observed in the polymerisation of propylene carried out on homogeneous catalysts containing bulky or chiral ligands. Thus, Ewen[6] showed that when sterically hindered ethylenebis(1-indenyl)titanium dichloride (a mixture of the meso form and racemate) was used as a catalyst for the polymerisation of propylene, there is the formation of 63% isotactic and 37% atactic polypropylene. If chiral ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride is used together with methylalumoxane $[AlMe-O-]_n$ as the co-catalyst, highly isotactic polypropylene is obtained.[183]

Table 3. Comparative activity of homogeneous ethylene polymerisation catalysts.[189]

System	Effective rate of polymerisation, litre mol^{-1} s^{-1}	Mole fraction of transition metal participating in the reaction
Cp_2ZrMe_2–MAO *	109 000	1
Cp_2TiCl_2–MAO	800	0.7
$TiCl_3 \cdot AlEt_2Cl$	2.7	0.005

*MAO = methylalumoxane.

Table 4. Polymerisation of C_2H_4 on different Zr systems.

Compound	Type of alumoxane	Activity, kg PE mol^{-1} h^{-1} bar^{-1}	T, °C
Cp_2ZrCl_2	Methylalumoxane	820	20
	"	242 000	80
$(Cp_2ZrCl)_2O$	"	203 000	80
Cp_2ZrMe_2	"	152 000	80
$Cp_2ZrCl(OBu)$	"	73 000	80
Cp_2ZrCl_2	Ethylalumoxane	2 100	60
Cp_2ZrMe_2	Tetraisobutylalumoxane	15 900	70

It is worth noting two studies[197,198] which are concerned with the preparation of high-molecular weight atactic polypropylene on homogeneous cene catalysts. Thus, by using bis(cyclopentadienyl)zirconium dichloride it is possible to obtain almost exclusively atactic polypropylene with molecular weights of up to 600 000. This type of polypropylene is characterised by a set of mechanical properties which is unusual for this polymer and may prove important for its use in producing seals, road and roof covers, and in a number of composite materials.

Chiral ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride cannot only be used to obtain isotactic polypropylene but also has polymerising activity which is 2–3 times higher than a catalyst on which only atactic polypropylene is formed. While the rates of polymerisation of ethylene and propylene on bis(cyclopentadienyl)zirconium compounds are 25 : 1, when this chiral catalyst is

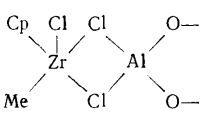
used this ratio is equal to 10:1.[187,188] These experimental results once again confirm the significant role played by steric factors during the polymerisation of α-olefins on homogeneous metal-complex systems.

With the same concentrations of monomers (pressure and polymerisation temperature) the factors which affect the activity of these catalysts are the degree of oligomerisation of the alumoxane and the concentrations of the catalytic components. The activity of the catalysts increases significantly as the concentration of zirconium decreases and the concentration of aluminium increases.[107]

The presence of methylalumoxane oligomer residues in very active homogeneous coordination catalysts for the polymerisation of α-olefins is unusual. The answer to this question will serve as a key for the preparation in future of new highly active catalytic systems.[184]

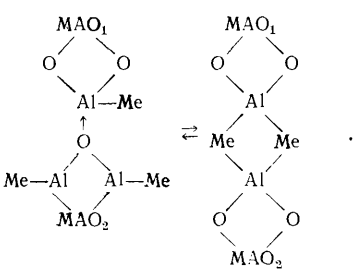
In a number of studies[199,200] particular attention is given to the role of alumoxanes in homogeneous metallocene catalytic systems. At one of the symposia on the relationship between the mechanism of heterogeneous and homogeneous catalysis, it was suggested for the polymerisation of α-olefins that alumoxanes can legitimately be regarded as a kind of support on which the active sites responsible for growth of the polymer chain are immobilised in a particular way.[81]

In an EPR study of the reactions that occur between a metallocene and methylalumoxane (MAO) it was found[84] that as a result of complexation and alkylation there was the formation of a compound with bridging bonds



Thus the proposal made previously about the similarity between alumoxane and a support is to a certain extent borne out. It is thought that when the metallocene reacts with MAO electron-deficient bridging complexes are formed and the bridging ligands are replaced by alkyls (from MAO) followed by elimination of the non-bridging groups as alkanes.

Consideration has been given to the probable establishment of an associative-dissociative equilibrium of MAO in which acid-base electron-deficient bridged complexes participate.

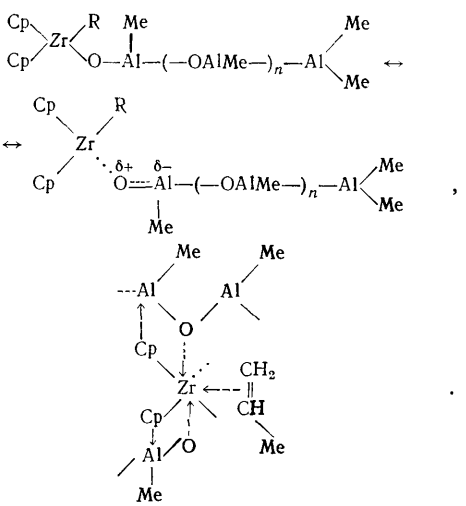


The catalytic sites deactivate each other in proportion to the concentration of Zr.[195]

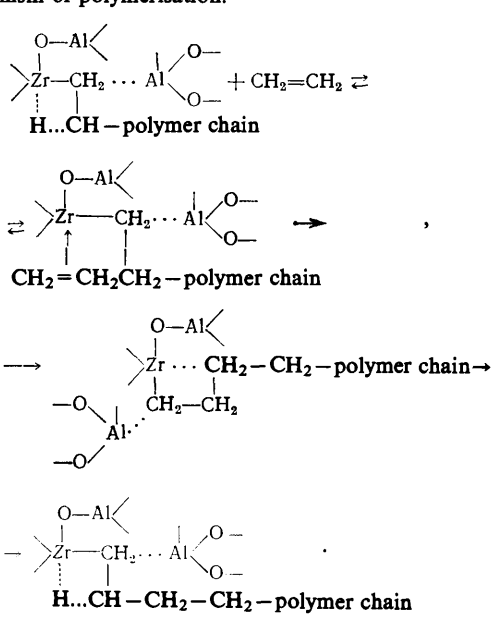
The theory advanced in this study[195] is confirmed experimentally in the observed relationship between the activity of the catalytic system and the content of Zr in it.

Despite the considerable number of theoretical and experimental studies, the most important of which were considered above, up to now there has been an absence of sufficiently reliable data on the structure and reaction mechanism of the active sites in homogeneous zirconocene catalytic systems containing alumoxanes. Recently fresh attempts were made to establish the details of the mechanism of polymerisation using carbonyl groups labelled on the carbon atom which are formed by treatment of the catalytic system with ^{14}CO.[185] However, because of a number of experiment difficulties which occurred, it was not possible to obtain sufficiently accurate results. Also, the use of CH_3OT as a label proved unacceptable.[185]

Nevertheless, proposals which do not contradict the experimental data have been made about the mechanism of complexation of a zirconocene compound with MAO, based on the electronic structure of the reacting components of catalytic system and monomer.[184,186] The essence of the proposed mechanism is as follows. On treatment with MAO polarisation of the π-electrons of the double bond in propylene occurs. As a result, a partial negative charge δ-arises on the carbon atom furthest from the methyl group. Because of this propylene is inserted into the polarised $Zr^{\delta+}-C^{\delta-}$ bond strictly stereospecifically.



The following scheme has been put forward to depict the possible mechanism of polymerisation:[190,200]



"Bridging" hydrogen is replaced by ethylene, which is initially π-bonded and then inserted into the Zr–C bond. This model

conforms with the hypothesis according to which chain growth is due to the existence of electron-deficient compounds in pentacoordinate bimetallic complexes.

An experimental study of the polymerisation of ethylene on these catalytic systems showed that the ligand environment of Zr has a significant effect on the yield and molecular weight of the resulting PE [201] (Table 5). It transpired that when MAO obtained by hydrolysis of $AlMe_3$ was used, a polymer with a lower value of $\overline{M}_n$ and wider molecular weight distribution is obtained.

Table 5. Effect of Cp substituent on the molecular weights and molecular weight distribution of polyethylene.[201]

Metallocenes	Yield, g PE $(g\ M)^{-1}\ h^{-1}\ atm^{-1}$	$MW \times 10^{-3}$	MW distribution
$(MeC_5H_4)_2ZrCl_2$	467	212	3.8
$(EtC_5H_4)_2ZrCl_2$	306	171	3.8
Cp_2ZrCl_2	252	140	3.5
$C_5Me_5ZrCl_2$	71	63	4.7

Table 6. Results of polymerisation on a TBP complex—MAO.[196]

Catalyst	Activity, g polymer $(g\ M)^{-1}\ h^{-1}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
Polymerisation of ethylene*			
(TBP)$TiCl_2$	228	360	2.0
(TBP)Ti(OPr-iso)$_2$	188	420	2.5
(TBP)Zr(OPr-iso)$_2$	6	—	—
Cp_2ZrCl_2	266	62	2.0
Polymerisation of propylene**			
(TBP)$TiCl_2$	186.0	800	2.2
(TBP)Ti(OPr-iso)$_2$	87.0	800	2.0
(TBP)Zr(OPr-iso)$_2$	0.2	380	2.4
Cp_2ZrCl_2	17.6	7.6	2.0
Ti(OPr-iso)$_4$	4.8	41.15	6.9

* Ethylene polymerisation conditions: amount of catalyst = 1.1×10^{-6} mol, MAO = 5.17 mmol, toluene = 10 ml, $P_{ethylene}$ = 1 atm, T = 20 °C, τ = 10 s.

** Propylene polymerisation conditions: amount of catalyst = 1.1×10^{-6} mol, MAO = 5.17 mmol, weight of propylene = 30 g, T = 20 °C, τ = 1 h.

Mention has already been made above of the polymerisation of propylene on homogeneous zirconocene-containing catalytic systems containing chiral ligands. Experimental data have recently been published on the preparation of stereoregular polypropylene using catalytic systems with the following structure:[202]

μ-X $(C_5H_2R^1R^2)_2ZrCl_2$, where

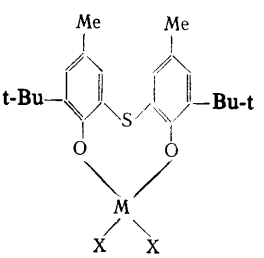
R^1 = t-Bu; R^2 = H; μ-X = $Me_2\overset{|}{C}-\overset{|}{C}Me_2$;

R^1 = t-Bu; R^2 = H; μ-X = Me_2Si  ;

R^1 = t-Bu; R^2 = Me; μ-X = Me_2Si  ;

R^1 = iso-Pr; R^2 = Me; μ-X = Me_2Si  .

There is considerable interest in titanium and zirconium compounds with a bidentate 2,2′-thiobis(6-t-butyl-4-methylphenoxy) ligand (TBP), which in combination with MAO exhibit extremely high activities in the polymerisation of olefins or styrene.[203,204] The catalytic systems



M = Ti, Zr;
X = Cl, OPr-iso;

in combination with MAO not only are highly active but also can be used to obtain polyethylene and stereoregular polypropylene with high molecular weights (Table 6).[196]

Interesting data on the microstructure of polypropylene were obtained when the homogeneous catalytic systems—$C_2H_4Ind_2.ZrCl_2$—MAO [205] and $C_2H_4(4,5,6,7\text{-}H_4Ind)_2ZrCl_2$ [206]—were used as the polymerisation catalyst. The resulting polypropylene contains units from both 1,2- and 1,3-addition.[207–209] It was established that the stereospecific action of the catalytic system decreases with an increase in temperature of polymerisation. The polymer obtained is completely soluble in the reaction medium, in contrast to the ordinary isotactic material. These types of polymers were called "anisotactic" by Rieger and Chien as distinguished from polypropylene obtained at a lower temperature.[209] The polypropylene which was soluble in acetone and ether is waxy, while the polymer isolated from hydrocarbon solutions will be more crystalline. Ishihara et al.[206,210] showed in the case of the polymerisation of styrene that by using zirconium and other similar catalytic systems it is possible to obtain hydrocarbon polymers with a syndiotactic structure. They used heterogeneous systems in combination with MAO, such as $Ti(OBu)_4/MAO/SiO_2$, as catalysts. It was established by Pellechia et al.[211–213] that an effective catalyst for the preparation of syndiotactic polystyrene has a low ratio of MAO to Ti. In other studies[211,212,214] an organozirconium system combined with MAO was used to obtain syndiotactic polystyrene. It should be mentioned that a similar catalytic system was tested in the polymerisation of 1,3-butadiene, isoprene, and 4-methyl-1,3-pentadiene.[215] The first two monomers gave the corresponding 1,4-*cis*-polymers, while the latter gave a 1,2-syndiotactic polymer. Catalytic hydrogenation of syndiotactic poly(1,2-[4-methyl-1,3-pentadiene]) resulted in the formation of crystalline poly(4-methyl-1-pentene) mainly with a syndiotactic microstructure and a softening point of 186 °C.[215]

Brinzinger[216] in an extension of studies on the stereospecific polymerisation of α-olefins with homogeneous metallocene catalysts synthesised and studied a number of chiral metallocenes with different structures and obtained from them active catalysts for the synthesis of isotactic polypropylene. Kaminsky et al.[217] successfully used chiral zirconocene compounds complexed with MAO for the copolymerisation of ethylene and propylene with other α-olefins.

As was mentioned above, MAO plays an important part in the polymerisation of olefins in which it participates. It is appropriate to mention that the addition of MAO to the catalytic system $Ti(OBu)_4/SiO_2$ markedly increases the activity of this system in the preparation of highly syndiotactic polystyrene.[218] However, the mechanism of this effect remains unclear. It is still not understood why the catalytic system consisting of Cp_2MCl_2 (M = Ti, Zr) and MAO, which is well known as an olefin polymerisation catalyst, is ineffective in the preparation of syndiotactic polystyrene, whereas the system $Ti(OPr)_4$–MAO, which is used to obtain syndiotactic polystyrene, also catalyses the polymerisation of olefins[219] but does not assist the copolymerisation of styrene and olefins.[220]

The effect of the nature of organozirconium and organoaluminium compounds on the properties of homogeneous catalytic systems for the polymerisation of α-olefins was also studied in the case of the homo- and co-polymerisation of ethylene with higher α-olefins on different organozirconium compounds.[220–222] The results of the investigation showed that the catalytic systems based on zirconocene combined MAO can be arranged in the following order of activity:

$$(C_5H_4SiMe_3)_2ZrCl_2 > Cp_2ZrCl_2 > (C_5H_4CH_2)_2ZrCl_2 >$$
$$> (C_5H_4Bu\text{-}t)_2ZrCl_2 > Ind_2ZrCl_2.$$

It has been suggested that the increase in catalytic activity of zirconocenes is in agreement with the increase in the electron-deficiency of the Zr atom in this series. This factor facilitates the reaction of the respective zirconocene with electron-donating MAO molecules.[142] However, a study of the reaction between the zirconocene dichloride derivatives $(C_5H_4SiMe_3)_3ZrCl_2$ or $(t\text{-}BuC_5H_4)_2ZrCl_2$ and MAO in an atmosphere of argon and ethylene using IR spectroscopy, and ^1H, ^{13}C, ^{27}Al, and ^{29}Si NMR [222] showed that the difference in the relative electronic effect from the alkyl groups is comparatively small. Taking into account the complexity of the catalytic system as a whole, it is difficult to accept that it is solely the electronic effect of the substituents in the Cp rings of zirconocenes that has a decisive role in the polymerisation process.

By studying the polymerisation of ethylene on the system $(RC_5H_4)_2ZrCl_2$–MAO, Nekhaeva et al.[221] found that a zirconium compound with an isopropyl substituent had a high activity (A_m), which cannot be due solely to the steric or electronic effect of this substituent

Substituents in Cp ring	H	Et	n-Pr	iso-Pr	$(iso\text{-}Pr)_2$
$A_m \times 10^{-6}$, g PE (mol M)$^{-1}$ h^{-1}	20.6	24.7	11.3	34.1	22.4

One of the factors that governs the high activity of the system with the isopropyl substituent would appear to be the development of hydride sites on the zirconium atom, in whose formation the hydrogen atoms of the α-carbon atom of the substituent participate.

Copolymers of ethylene containing from 1 to 10% of vinylcyclohexane, 4-methyl-1-pentene, and 3-methyl-1-butene were obtained on the same catalysts.[178,194]

Quite recently a very interesting report[223] was published on the use of a homogeneous catalytic system to synthesise polypropylenes with different structures depending on the experimental conditions—from stereoregular crystalline structures to amorphous products which were thermoplastic elastomers. This suggests the possibility of producing from the same hydrocarbon monomer various structural modifications which have a different set of mechanical and industrial properties.

The experimental data examined above show that the use of homogeneous metal-complex catalytic systems for the polymerisation of olefins can be used to obtain polyolefins with different structures. There is no doubt that this area will be developed further and will be extended not only to linear but also to branched higher α-olefins. There is a future for them in resolving the main scientific and practical problem—the directed synthesis of polymer structures with a given set of properties.

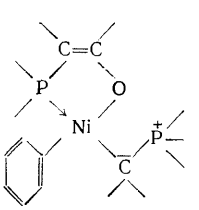
3. Catalysis based on organometallic lanthanide compounds

Fairly recently the first studies were published[223–228] on metal-complex catalytic systems containing organic compounds of metals of the lanthanide group, in particular neodymium. Particular attention was given to this question by Chinese research workers[229] who studied the stereospecific polymerisation of the dienes—butadiene and isoprene. Lanthanide catalytic systems have attracted the attention of research workers because of their high stereospecificity and also by the fact that in using them the possibility of oligomers being formed, which usually occurs when polydienes are being prepared in the presence of other metal-complex systems, is excluded. Thus, the absence of oligomers is of considerable importance in the development of an ecologically clean technology for obtaining stereoregular polyisoprene.[230]

Attention has also been drawn[230–233] to the future potential in using such catalytic systems in the polymerisation of α-olefins.[234] Thus the copolymerisation of α-olefins with methyl acrylate on organometallic ytterbium compounds has been reported by Japanese authors.[235,236] This opens up the possibility of carrying out the copolymerisation of olefins with polar monomers, which had previously been virtually impossible because of the "poisoning" of the active sites of the catalyst by the polar monomers.

4. Ylide polymerisation catalysts

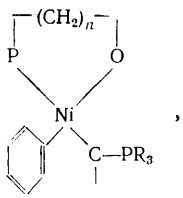
Interesting possibilities for obtaining linear and branched polyethylene are opened up by using recently proposed ylide nickel complexes as catalysts.[156,157,237] It is assumed[238] that in this type of catalyst the following coordinate structural residues occur:



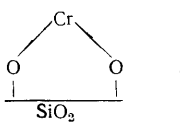
Linear polyethylene has been obtained with the use of this catalyst.

In an alternative method, two successive processes—the oligomerisation of ethylene to oligomeric α-olefins and the subsequent copolymerisation of them with the initial ethylene—can be carried out on the ylide catalyst. In this case LLDPE-type polyethylene is formed.[239] In order to carry out this process, bis(ylido)nickel catalytic systems are used in combination with a heterogeneous chromium catalyst, which function successfully in the absence of aluminium alkyls as co-catalysts.[240] In this residue the nickel complex is immobilised on the chromium catalyst, and a new

active bifunctional catalyst for the polymerisation of ethylene is formed, consisting of two components, one of which causes the oligomerisation reaction and the other causes copolymerisation of the α-olefins (C_6-C_3) formed at the first stage with ethylene:
oligomerisation:

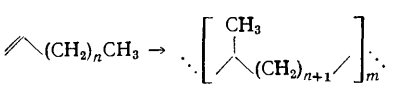


polymerisation:



By controlling the ratio of Ni to Cr and the polymerisation temperature it is possible within certain limits to change the degree of branching of PE and the length of these branches in the desired direction.

Mention should also be made of one nickel catalyst with which a novel type of polymerisation of α-olefins can be carried out. This refers to a homogeneous complex of nickel with a phosphorane ligand — bis(trimethylsilyl)aminobis(trimethylsilylimino) phosphorane.[241] Polymerisation of both linear and branched α-olefins occurs on this catalyst. The structure of the resulting poly(α-olefins) is unusual. It a linear α-olefin participates in polymerisation the polyolefin contains only one methyl branch separated by given segments of the polymer chain:



IV. Emergence of new possibilities for the development of highly effective metal-complex catalytic systems

Above we examined the main areas of metal-complex catalysis of the polymerisation of olefins that have undergone rapid development in recent years. Naturally this review has not covered all of the publications in this area, but from the results that it contains the reader can, in our opinion, form a sufficient idea of the state of this problem.

Nevertheless we thought it necessary in conclusion to draw attention to the future, and from our viewpoint, most fruitful methods of developing metal-complex catalysis in relation to the polymerisation of α-olefins.

Cossee,[242] who attempted to reveal the nature of the active sites of transition metal complexes in the polymerisation of α-olefins, showed how the metal–carbon bond (the alkyl group of α-olefins) is preserved throughout the whole reaction cycle, with the energy losses in the strength of this bond not exceeding 20% and being fully compensated by the formation of a new bond during polymerisation.

The reactions which occur in this manner can legitimately be classed as concerted reactions, which are characterised by a synchronous redistribution of electron density in the bonds, giving rise to low values of the energy of activation.[23,24]

In this respect metal-complex catalysis is similar to enzyme reactions, which also take place via the formation of intermediates and are classed as reactions that occur with a concerted mechanism. A new bond is formed in these reactions at the same time as the destruction of the old one, which helps to stabilise the transition state and accelerates the reaction.

In terms of stereoselectivity and mechanistic action there is also a certain similarity between metal-complex catalysis (in particular the polymerisation of α-olefins) and enzyme catalysis. In both cases the concerted reactions occur under mild conditions, in non-polar solvents, and at high rates. It should be noted here that the high rates that are typical for enzyme reactions have so far not been reached in metal-complex catalysis. It may be assumed that this is due to the fact that the degree of concertedness which occurs in enzyme catalysis has so far been achieved in metal-complex catalysis. It is not excluded that the required degree of concertedness can be achieved through new catalytic systems as well as through the use of reaction equipment which ensures that the reaction occurs only in the kinetic region.

Research and development on catalytic systems containing several transition metals with a different ligand environment should also prove to have future potential.

It is to be expected that new lanthanide metal-complex catalysts will be synthesised for the preparation of copolymers of α-olefins with polar monomers. At the present time only the high-pressure radical copolymerisation of ethylene with vinyl acetate and acrylic monomers is known.

The development of microheterogeneous catalytic systems has future potential. The idea for developing such catalysts is derived from the fact that high-molecular weight compounds in solution that are not cross-linked form threads which comprise macromolecules with a high content of solvent in them. On particles like this that are not cross-linked it is possible to fix in a specific way virtually any transition metal complexes whose active sites are responsible for growth of the polymer chain. Microheterogeneous catalysts are most readily designed in a form that has the greatest resemblance to enzymes. Such microheterogeneous catalysts have already been used with considerable effectiveness in hydrogenation and hydroformylation, for example. However up to the present time there has been no information on the use of such catalysts in polymerisation processes.

Interesting effects can be expected from the use of surfactants in metal-complex catalysis of polymerisation. When present in concentrations above the critical micelle concentration, surfactants are known to have colloidal properties. In a number of cases the rate constants of the reactions that occur with the participation of such micellar solutions of surfactants increase by several orders, which is due to concentration and orientation effects. There is reason to believe that these effects can also be achieved when surfactants are used in the metal-complex catalysis of polymerisation processes. In this case there is the possibility of bringing together the existing methods of ionic coordination polymerisation of olefins and emulsion polymerisation methods. There is the so-called micellar polymerisation catalysis, which in certain cases can be of definite practical interest.

Finally, the use of heterogenised cluster transition metal complexes in the polymerisation of α-olefins is attractive. There is every reason to expect a combination of high effectiveness and the necessary stereospecific action for such catalysts. It is therefore

necessary to bear in mind the possibility of achieving the introduction of microcluster transition metals into zeolites (serving as supports). On the surface the atoms of this type of microcluster have free valence bonds which make these atoms unusually reactive. A systematic investigation of cluster catalysts, including fairly complex physical methods for studying three-dimensional cluster lattices, is required for progress in the use of these catalysts.

It is probable that the trends in extensive scientific research into the improvement of existing methods and the development of fundamentally new methods in the interesting area of metal-complex polymerisation catalysis are not restricted to the examples considered here.

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